ANION ADSORPTION IN HAWAIIAN SOILS

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By

Toshio Mekaru

Thesis Committee:

Goro Uehara, Chairman
Robert L. Fox
Ukio Urata

We certify that we have read this thesis and that in our opinion it is satisfactory in scope and quality as a thesis for the degree of Master of Science in Soil Science.

THESIS COMMITTEE

Gora Uehara
Chairman

Ikio Ikata

Robert L. Fox

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INTRODUCTION

Anion adsorption generally occurs to a greater extent, and therefore plays a more important role in plant nutrition and soil behavior in tropical soils than in soils of the temperate regions. Higher anion adsorption in tropical soils is attributed to their larger iron and aluminum oxide contents relative to temperate region soils. In Hawaii, for example, it is not uncommon to measure 20 to 40 percent free iron oxide in agriculturally productive soils. High crop yields however are obtained only by large applications of phosphate fertilizer. Frequently crop response to phosphorus application is obtained even when fertilizer application exceeds 1000 pounds elemental phosphorus per acre.

As a rule, soils which require high phosphate fertilization are those with high iron and aluminum oxide contents. In certain of these soils large increases in sugar cane yields have been obtained by additions of calcium silicate. Although the exact cause for this increased yield is not clearly understood, there is reason to believe that the special character of the silicate anion plays an important role in altering the surface chemistry of these soils.

As a general rule Hawaiian soils appear to be able to adsorb more anionic constituents than other soils. Two obvious cases are high phosphate requirements of soils and the response of crops to silicate applications. A less well known example is the high molybdenum requirements of these soils (Younge and Takahashi, 1953). Fox et al. (1965) have shown that the sulfate sulfur content of Hawaiian soils is very high when compared to data collected from the Midwestern United States.

Hawaiian soils also appear to have adsorbed high amounts of arsenate weed killers. Evidence for high selenium content in Hawaiian soils have been reported, but plants growing on these were shown to be low in this element.

The purpose of this study was to determine the magnitudes of anion adsorption in Hawaiian soils and to arrive at a rational explanation for the occurrence of this important phenomenon in ferruginous Hawaiian soils.

REVIEW OF LITERATURE

The study of anion adsorption by soil materials began in earnest about 1927 when Mattson and his colleagues (1927 to 1937) began publishing a series of papers on this subject. Mattson used sesquioxide gels as one of his absorbate and essentially predicted much of what is observed in anion adsorption today. Modern reports on the same subject differ only on the mechanism of anion adsorption.

Mattson's work was largely forgotten in the intervening period as the result of the practical applications of X-ray diffraction analysis to soil colloids and the discovery that soil colloids were largely crystalline silicate minerals. A rational explanation for cation exchange phenomenon and the inability to discover an analogous phenomenon in anion exchange played a role in reducing interest in the latter. Much of this can be attributed to the disproportionate research efforts conducted in temperate zones where anion adsorption is comparatively unimportant.

It is generally agreed that hydrous oxides of iron and aluminum are the soil constituents mainly responsible for anion adsorption. Soils occurring in temperate regions rarely contain more than 5 percent free iron oxide. For example, Kemper and Koch (1966) in their analysis of several hundred soils from Canada and the Western United States report a maximum value of 5 percent free iron oxide.

Published reports on anion adsorption have generally come from three regions in the United States. They are the northeast which include soils such as the Caribou which is known for high phosphate adsorption capacity, the southeast with soils such as the Cecil,

Davidson and Aiken series and the northeast with the Quillayute, Astoria and Aiken series. These soils have one common feature, namely a high iron oxide content. Compared to soils in Hawaii which rarely contain less than 5 percent free iron oxide, the free Fe_2O_3 content of the temperate climate soils must be considered low oxide soils by comparison.

The review of literature will be confined to a limited number of recent publications which the author feels adds much to the understanding of anion adsorption. Although there are other earlier papers on the same subject, one can begin with a report by Parks and de Bruyn (1962) in which they describe a method for obtaining the zero point of charge (hereafter referred to as ZPC) of hematite. According to Parks and de Bruyn the surface charge of hematite can be negative, zero or positive depending on the proportion of hydrogen or hydroxyl ions adsorbed on its surface. The pH at which the surface density of adsorbed hydrogen ion equals the density of adsorbed hydroxyl ion is referred to as the ZPC. At pH's lower than the ZPC the surface possesses a net positive charge, and at higher pH values, the surface acquires a net negative charge. Figure 1 illustrates the pH dependent charge of hematite. The ZPC is also the iso-electric point if hydrogen and hydroxyl ions are the charge or potential determining ions. The ZPC is not always equivalent to the iso-electric point for there are many cases in which the ZPC is independent of pH.

Schofield (1949) expressed this same concept by referring to the acquisition of positive charge as proton acceptance and acquisition of negative charge as proton transfer away from the surface.

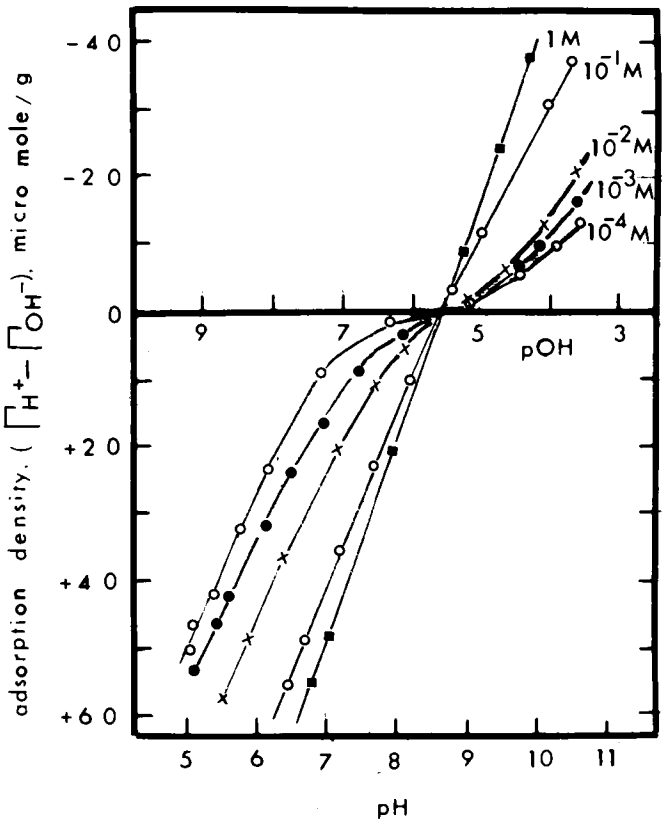

FIGURE 1. ADSORPTION DENSITY OF POTENTIAL DETERMINING IONS ON HEMATITE AS A FUNCTION OF pH AND IONIC STRENGTH OF INDIFFERENT ELECTROLYTE (KNO_3). (SOURCE: PARKS AND DE BRUYN, 1962.)

According to the data of Parks and de Bruyn, zero point of charge for hematite occurs at pH 8.5. The average ZPC of six different hematite samples compiled by Atkinson et al. (1967) was pH 8.77. Atkinson et al. also measured a ZPC of pH 7.55 for goethite. Yopps and Fuerstenau (1964) measured a ZPC of pH 9.1 for alfa-alumina and listed ZPC for a number of hydroxides and oxides of alumina.

The zero point of charge has some significance in anion adsorption, since one would expect higher adsorption when pH is lower than the ZPC. Higher adsorption of anions in acid ferruginous soils is a well known phenomenon in the tropics.

It turns out however that anion adsorption is a much more complicated process. In the case of hydrous oxide and oxide of iron and aluminum the potential determining ions are hydrogen and hydroxyl ions. These ions are adsorbed in the inner Helmholtz plane (IHP) of the double layer and are said to be adsorbed specifically (Hingston et al., 1967; Atkinson et al., 1967). Parks and de Bruyn (1962) suggest that adsorption of hydroxyl ions on oxide surface is unlikely for this would require that the coordination number of Fe (III) be changed from 6 to 7. Instead proton transfer away from the oxide surface is proposed as more likely. The positive charge which develops from H^+ adsorption can be satisfied by counter ions such as Cl^- or NO_3^-. One would expect adsorption of non-specifically adsorbed Cl^- and NO_3^- to cease when the ZPC is attained. Quirk (1960) presents data which show cessation of pH dependent Cl^- adsorption on kaolinite surface at a pH of 7.0. This suggests that kaolinite has a ZPC near pH 7.0. Hingston et al. (1968) show very clearly that chloride adsorption ceases at pH 8.0 for

goethite. This pH was very close to the ZPC of goethite reported earlier by Atkinson et al. (1967).

In the case of H_3SeO_3, H_3AsO_4, H_3PO_4, $H_4P_2O_7$, $H_5P_3O_{10}$ and H_4SiO_4, anions of these acids continued to be adsorbed beyond the pH where Cl^- adsorption ended. Hingston et al. (1967) suggest that selenate, arsenate phosphate, polyphosphate and silicate ions are specifically adsorbed and that this type of adsorption involves displacement of hydroxyl ions coordinated to iron or aluminum. The displacement, they say, is a ligand exchange process.

Figure 2 illustrates chloride ion adsorption. When the surface acquires a net positive charge, positive adsorption of chloride and negative adsorption of cations would be expected to occur.

In Figure 3 phosphate adsorption is viewed as a ligand exchange process. According to Hingston et al. (1967, 1968), adsorption of phosphate increases the net negative charge of oxide surfaces. Increase in negative charge should result in a measurable rise in cation exchange capacity of phosphated soils. Toth (1937), Davis (1945) and Coleman and Mehlich (1948) have reported such increases in cation exchange capacities.

Hingston et al. (1967) present data to show that additions of specifically adsorbed anions shifts the ZPC of iron oxides to lower pH values. Figure 4 illustrates a hypothetical oxide in which the ZPC is shifted progressively to lower pH as increasing amount of phosphate is added. Note that for a particular pH, the higher the phosphate adsorbed the greater the net negative charge. This model

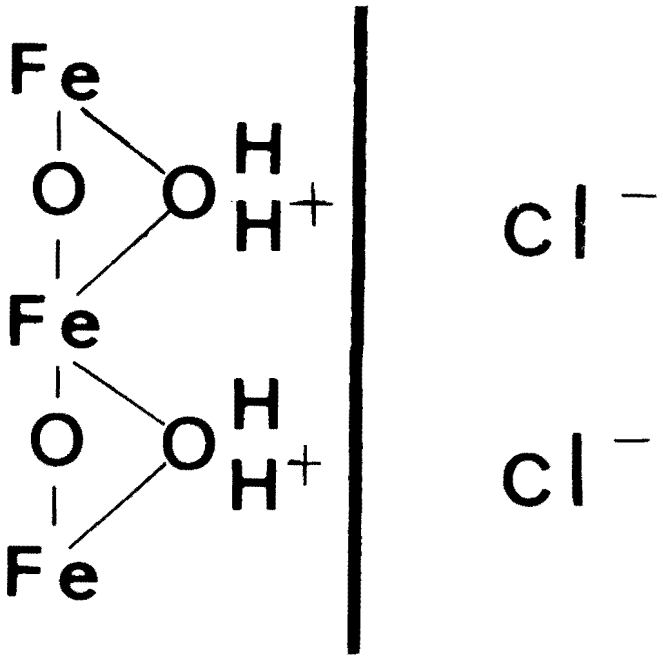

FIGURE 2. PROBABLE MECHANISM FOR Cl^- ADSORPTION IN pH RANGE BELOW THE ZERO POINT OF CHARGE. POSITIVE HYDROGEN IONS ARE SPECIFICALLY ADSORBED IN THE INNER HELMHOLTZ PLANE AND CHLORIDE ION ARE ADSORBED NON-SPECIFICALLY AS COUNTER IONS.

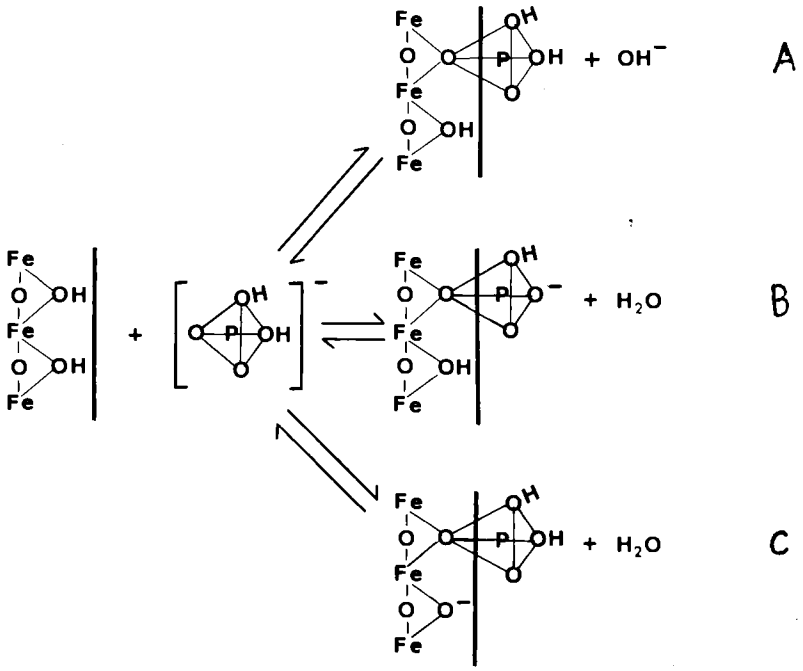

FIGURE 3. PROBABLE MECHANISM OF PHOSPHATE ADSORPTION. pH INCREASE IS PREDICTED BY (A) BUT NOT BY (B) OR (C). IN (B) THE SURFACE ACQUIRES A NEGATIVE CHARGE BY PROTON TRANSFER BY THE SORBED PHOSPHATE, WHEREAS IN (C) THE NEGATIVE CHARGE ARISES FROM PROTON TRANSFER DIRECTLY FROM SURFACE HYDROXYL.

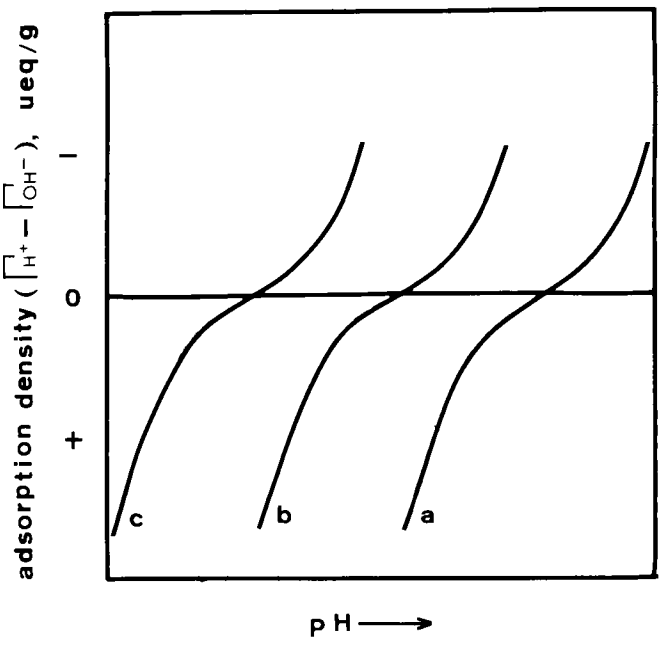

FIGURE 4. HYPOTHETICAL CURVES ILLUSTRATING THE INFLUENCE OF ANION ADSORPTION ON THE ZERO POINT OF CHARGE OF AN OXIDE. THE ZERO POINT OF CHARGE FOR THE PURE OXIDE (a) IS PROGRESSIVELY DISPLACED TO LOWER pH'S AS MORE ANIONS (c > b) ARE ADSORBED.

accounts for the increased cation exchange capacity of phosphated soil reported by earlier workers.

The works of Parks and de Bruyn (1962), Yopps and Furstenau (1964) and Atkinson et al. (1967) all show that at constant surface charge the pH of an oxide suspension is clearly a function of the indifferent electrolyte concentration of the suspension. Their results show that whether the pH increases, decreases or remains constant when the indifferent electrolyte concentration is increased, depends upon whether the oxide surface possesses a net positive, net negative or net zero charge, respectively.

In routine soil analysis pH is often measured in water and in KCl solution. A quantity called delta pH ($\triangle$pH) where,

$$\triangle pH = pH_{KCl} - pH_{H_2O}$$

is used to determine the net charge of a soil material. If the $\triangle$pH is positive as is sometimes the case in high oxide soils, the soil is said to have a net positive charge. On the basis of the work of Parks and de Bruyn (1962) and Atkinson et al. (1967) we now know that for any given oxide soil, $\triangle$pH can take on any value depending on the pH. One can also anticipate that a phosphated soil will give a more negative $\triangle$pH than a non-phosphated soil at the same pH.

Another important consequence of the ligand exchange model of anion adsorption is that this model allows for adsorption of specifically adsorbed anions (e.g., $PO_4^{\equiv}$, $SO_4^{=}$, $A_sO_4^{\equiv}$, etc.) even when the colloid surface possesses a net negative charge.

Harward and Reisenauer (1966) appear to have been the first workers to explicitly state the case for ligand exchange in anion

adsorption mechanism. However, they failed to recognize the difference between specific and non-specific anion adsorption.

MATERIALS AND METHODS

A. Soils

Twelve soil series were selected as test samples. Seven of these were collected from the Island of Hawaii and were chosen to represent a climo-sequence of soils developed from volcanic ash. Five other soils from the Island of Oahu were chosen to represent soil developed from basalt and/or alluvium. Soils used in this study are tabulated in Table I. A description of each soil can be found in the "Soil Survey of the Territory of Hawaii" (Cline, 1955).

B. Methods[1/]

1. Sulfate adsorption isotherm

The amount of sulfate adsorbed by a soil was determined by difference. For example, 2.5 grams of Akaka soil on an oven-dry basis and weighing 12.8 grams on a field moisture basis were placed in a 100 ml, polyethylene centrifuge tube. To this 25 ml of 0.1N K_2SO_4 solution was added and the mixture thoroughly shaken in a mechanical shaker for 1 hour and then allowed to stand for another 3 hours or longer. Just prior to centrifugation the suspension was again shaken for 10 minutes. A portion of the suspension was transferred to a 50 ml polyethylene centrifuge tube and centrifuged at 16,000 RPM's for

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[1/] All samples were stored in plastic bags to prevent soils from undergoing excessive drying.

TABLE I. SOILS USED.

Soil Series	Old Classification	New Classification	
	Great Soil Group	Family Level	Sub-Group
		VOLCANIC ASH	
Akaka	Hydrol Humic Latosol	thixotropic, isomesic	Typic Hydrandept
Hilo	Hydrol Humic Latosol	thixotropic, isohyperthermic	Typic Hydrandept
Honokaa	Hydrol Humic Latosol	thixotropic isothermic	Typic Hydrandept
Waimea	Reddish Prairie	ashy isothermic	Typic Eutrandept
Pahala (Naalehu)	Reddish Prairie	ashy isohyperthermic	Typic Eutrandept
Waikaloa	Reddish Brown	ashy isothermic	Ustollic Eutrandept
Kawaihae	Red Desert	ashy isohyperthermic	Typic Vitrandept
		BASALT OR ALLUVIUM	
Paaloa	Humic Latosol	clayey, oxidic isothermic	Humoxic Tropohumult
Kolekole	Humic Ferruginous Latosol	fine-silty oxidic, isothermic	Oxic Humitropept
Wahiawa	Low Humic Latosol	clayey, halloysitic isothermic	Tropeptic
Molokai	Low Humic Latosol	fine-silty, halloysitic isohyperthermic	Tropeptic
Lualualei	Dark Magnesium clay	montmorillonitic, isohyperthermic	Typic chromustert

10 minutes. The supernatant liquid was analyzed for sulfate by the turbidimetric method described by Bardsley and Lancaster (1965). The reduction in sulfate ion concentration in the supernatant liquid results from adsorption, and by dilution with soil moisture. The latter factor was taken into account in computing adsorbed sulfate.

Since adsorbed sulfate is determined by difference, the accuracy of this method diminishes as the difference approaches small values. This problem arises in the high concentration range, and also in the low concentration range for samples with low sulfate adsorption capacities. For the latter reason sample size was varied accordingly.

For adsorption capacities between 0 to 10, 10 to 25 and greater than 30 me/100 grams soil, sample size was respectively adjusted to 10, 5, and 2.5 grams on an oven-dry basis.

2. Sulfate adsorption isotherm of KCl-washed samples

Native sulfates interfere with adsorption of added anion. It was soon learned that sulfate adsorption, if it is to represent adsorption capacity of a soil, must be freed of its native adsorbed sulfate. Native sulfate was removed by washing with 50 ml increments of 2N KCl solution in a 100 ml centrifuge tube. This procedure was repeated until little or no $SO_4^=$ ion could be detected in the supernatant liquid. For example, 5 washings were necessary to free a Wahiawa sample of $SO_4^=$, whereas 10 to 15 washings were required in the Hilo and Akaka soils.

The KCl-washed sample was washed twice with water to remove excess electrolyte. Further washings often resulted in dispersion. Sulfate adsorption was always higher in a KCl-washed sample than in the natural unwashed samples.

In the KCl-washing procedure, use of a superspeed centrifuge is not recommended because the settled soil is compacted beyond easy redispersion.

3. Sulfate adsorption isotherm of KCl-washed and dialyzed samples

To free the KCl-washed samples of chloride ion, selected samples were dialyzed. After dialysis, several samples were tested for adsorbed chloride by extraction with K_2SO_4 solution, and were found to be chloride free. Sulfate adsorption was lower in the dialyzed sample than in the KCl-washed samples.

4. Nitrate adsorption isotherms

Nitrate adsorption isotherms were obtained on selected samples using KNO_3. The amount of nitrate adsorbed was determined by difference, similar to the procedure for sulfate adsorption. Nitrate was determined by a method described by Bremner (1965).

5. Phosphate adsorption isotherms

Phosphorus adsorption for the Kolekole, Wahiawa, Hilo and Akaka samples were determined by using $NaH_2PO_4 \cdot H_2O$, $Na_2HPO_4 \cdot 7H_2O$ and $Na_3PO_4 \cdot 12H_2O$ to measure the effects of pH on phosphate adsorption. All measurements were made on natural, untreated soils. Sample sizes were 10 and 2.5 grams, respectively, for the Kolekole-Wahiawa and the Hilo-Akaka samples. After shaking

vigorously for 1 hour and equilibrating for another 11 hours, adsorbed phosphate was determined by difference.

6. Extraction of native sulfate

Native sulfate was extracted with water, 2N KCl solution and 0.05N KH_2PO_4 solution. Each test sample was washed with 50 ml increments of the extractant in a 100 ml centrifuge tube. Each sample received a 10 minute shaking before centrifugation. Sample sizes were 2.5 and 10 grams, respectively, for the Hilo-Akaka and Wahiawa-Kolekole soils. The supernatant liquid before addition of barium chloride was used as a blank. Phosphorus interference was prevented by adding 1 ml of 6N HCl when phosphate was used as an extractant. In the case of KCl extraction, the same amount of KCl solution was added to the standard solution. Table II shows the amount of sulfate sulfur extracted by the three extraction procedures.

Native sulfate contents for all samples were determined by extracting each sample with four increments of 50 ml solution containing 2.5 me of $PO_4^{\equiv}$ as KH_2PO_4 and 10 me of KCl. The KCl was added to prevent dispersion and reduce solution discoloration. The sample was centrifuged at less than 1800 RPM to prevent the sample from becoming compacted at the bottom of the centrifuge tube. Since the aliquot used was lower in high sulfate samples, the standard curve was adjusted to contain the same phosphate and KCl concentration as the sample solution.

TABLE II. SULFATE SULFUR CONTENT EXTRACTED BY WATER, 2N KCl AND 0.05N KH_2PO_4 SOLUTION.

Soil	No. of Extractions	H_2O $SO_4^=$ me/100	2N KCl $SO_4^=$ me/100 g	0.05N KH_2PO_4 $SO_4^=$ me/100 g
Wahiawa (3)	1	0.118	not determined	0.737
	2	0.1	" "	0.393
	3	0.076	" "	0.143
	4	0.062	" "	0.075
	5	0.043	" "	0.064
	Total $SO_4^=$	0.399	1.60	1.41
Kolekole (5)	1	-	0.225	0.293
	2	-	0.121	0.137
	3	-	0.061	0.037
	Total $SO_4^=$	-	0.408	0.467
Hilo (I-4)	1	-	3.53	8.38
	2	-	1.68	3.00
	3	-	1.04	1.18
	4	-	0.62	0.57
	5	-	0.62	0.27
	6	-	0.51	trace
	Total $SO_4^=$	-	8.00	13.4
Akaka (I-5)	1	trace	not determined	16.4
	2	"	" "	11.87
	3	"	" "	2.8
	4	"	" "	0.93
	5	"	" "	0.0
	Total $SO_4^=$	.3	25.0*	32.0

*Sixteen extractions.

7. Maximum sulfate adsorption capacity

Three methods for determining maximum sulfate adsorption were compared. These methods will henceforth be referred to as Water, Acetone-water and Modified Schofield methods.

a. Water method

Samples were washed three times with 50 ml increment of K_2SO_4 solution (0.3N for Hilo and Akaka soils and 0.04N for Wahiawa and Kolekole soils) in 100 ml centrifuge tubes. Since native sulfate was not desorbed in significant amounts by water, excess electrolyte was removed by washing with three 50 ml increments of distilled water. Adsorbed sulfate was extracted with 50 ml increments of KH_2PO_4-KCl solution described in procedure 6. The accumulated extract was placed in 250 ml volumetric flasks and made to volume. Approximately 25 ml of the extract was placed in a 50 ml polyethylene tube and centrifuged at 16,000 RPM for 10 minutes to remove suspended solids. From this 5 to 20 ml, depending on $SO_4^{=}$ content, were transferred to a 50 ml volumetric flask. To this, 1 ml of 6N HCl was added to reduce phosphate interference in sulfate determination.

b. Acetone-water method

This method was identical to the water method except a 1:1 acetone water mixture was used to remove excess electrolyte.

In a number of cases dispersion was a serious problem and sample size was reduced from 10 to 5 grams so that

the superspeed centrifuge could be used. This, however, had the disadvantage of making the settled soil difficult to redisperse. The compacted material was loosened with a long, horn spatula and thoroughly crushed. After washing with acetone-H_2O solution, the adsorbed $SO_4^=$ was extracted by a phosphorus-KCl solution described in procedure 6. The sample was centrifuged at a lower speed (1800 RPM).

c. Modified Schofield method

Schofield's (1949) method involves washing a sample with a salt solution until no further adsorption is noticeable. Once equilibrium is attained the supernatant liquid is decanted. The adsorbate in both adsorbed and solution phase is removed by extraction with another electrolyte and the adsorbed ion computed from the expression

Adsorbed sulfate = Total sulfate conc. - conc. in soln. (I)

In the modified Schofield method employed in this study, the saturating solution was K_2SO_4 as in the water and acetone-water method. The replacing solution was 0.05N KH_2PO_4 - 0.2N KCl solution. The essential difference between this method and the two previously described methods is in the way excess electrolyte was handled. In the first two methods excess electrolyte was physically removed, whereas, the Schofield method accounts for it by difference.

A comparison of maximum sulfate adsorption using the three methods is shown in Table III.

8. CEC increase with phosphorus adsorption

Samples (10 g for Wahiawa (3) and 2.5 g for Hilo (I-4)) were equilibrated for 12 hours with 25 ml of phosphorus ($NaH_2PO_4 \cdot H_2O$ or $Na_2HPO_4 \cdot 7H_2O$) solution of varying concentrations. Each sample was centrifuged at 1800 RPM for 10 minutes. Phosphorus content was determined in the supernatant liquid and the amount of adsorbed phosphorus was computed from the techniques given in procedure 7c. The sample was then NH_4-ion-saturated by washing with four increments of 50 ml 1N NH_4OAc solution adjusted to pH 7.0. Phosphorus desorbed during NH_4OAc saturation was reduced from original phosphorus adsorbed to compute net phosphorus adsorbed. The soil was subsequently washed with four increments of 50 ml methyl alcohol to remove excess NH_4OAc. NH_4^+ was extracted by washing with 1N KCl solution. Exchangeable NH_4^+ was determined by the Bremner method. The increase in CEC per millimole of net adsorbed phosphorus $\left(\frac{\Delta \text{ CEC}}{\text{P (m mole)}}\right)$ was computed.

9. Influence of pH on $\frac{\Delta \text{ CEC}}{\text{P (m mole)}}$

The procedure described in the previous section was designed to evaluate increasing cation exchange capacity with increasing phosphate adsorption. The procedure in this section was developed to evaluate the effect of pH on $\frac{\Delta \text{ CEC}}{\text{P (m mole)}}$. This was accomplished by measuring CEC of a phosphated soil

TABLE III. COMPARISON OF THE WATER, ACETONE-WATER AND MODIFIED SCHOFIELD METHODS FOR DETERMINING MAXIMUM SULFATE ADSORPTION (ME/100 G). THE pH REPRESENTS THE VALUE AFTER EQUILIBRATION WITH K_2SO_4.

Soil	H_2O Washing	Acetone-H_2O Washing	Modified Schofield Method	Sulfate Isotherm using KCl Washed Soil	pH
Wahiawa (3)	1.8	3.9	3.1	2.2	4.51
Kolekole (5)	1.0	2.8	2.7	-	4.40
Hilo (I-4)	18.2	34.0	34.1	29.0	6.91
Akaka (I-5)	41.8	58.1	56.5	49.0	6.30

using NH_4OAc solution adjusted to pH 5.36, 7.0 and 8.4. A similar change in CEC for the nonphosphated soil was also measured. The difference in the CEC at each pH for phosphated and nonphosphated sample was referred to as "Net CEC Increase."

10. Delta pH ($\triangle$pH) determination

Soil pH was measured in a paste prepared with water and also with 1N KCl solution. Delta pH (hereafter referred to as $\triangle$pH) was defined as

$$\triangle pH = pH_{KCl} - pH_{H_2O}$$

or the pH difference between pastes prepared with 1N KCl and with water. The value of $\triangle$pH was also measured in paste prepared with 1N K_2SO_4.

11. Interaction between anions

a. Isoconcentration isotherm

These experiments were designed to measure the effect of one anion on the adsorption of another. The total anion concentration was held constant but the proportion was varied.

The sulfate-chloride interaction was measured on untreated Kolekole (5) and Hilo (I-4) soils. Twenty-five ml of 0.2N solution containing sulfate and chloride in ratios 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0 were added to 2.5 grams of Hilo soil and 10.0 grams in the Kolekole sample. The adsorption of sulfate was measured and the data plotted with milliequivalent of $SO_4^{=}$ adsorbed per 100

grams soil on the vertical axes and milliequivalent $SO_4^{=}$ added per 100 grams soil on the horizontal axes.

A similar analysis was carried on a KCl-washed and dialyzed Akaka (I-5) sample using a solution containing 2.5 me of nitrate-chloride mixture in one case and nitrate-sulfate mixture in another. In each case the quantity of nitrate adsorbed was measured.

b. Sulfate-nitrate interaction

In this experiment the concentration of one anion was kept constant and the concentration of the other anion was varied as follows:

NO_3^- (me/2.5 g)	$SO_4^{=}$ (me/2.5 g)	$SO_4^{=}$ (me/2.5 g)	NO_3^- (me/2.5 g)
0.5	0.5	0.5	0.5
0.5	5.0	0.5	5.0
0.5	12.5	0.5	12.5
0.5	25.0	0.5	25.0

A dialyzed Akaka (I-5) sample was used, and in each case the anion whose cocentration was maintained constant was analyzed.

RESULTS AND DISCUSSION

A. Delta pH ($\triangle$pH)

Consider two systems, the first a hydrogen saturated cation exchanger and the second a hydroxyl saturated anion exchanger. The pH in water would be acid in the first and alkaline in the second. If the pH's of both are again measured in a normal solution of a neutral salt such as K_2SO_4 or KCl, the pH would be more acid in the cation exchanger and more alkaline in the anion exchanger compared to the pH's measured in water.

Consider now an ion exchanger with both cation and anion exchange sites saturated with hydrogen and hydroxyl ions, respectively. If the ratio of CEC to AEC for this material is much greater than unity, the pH in the salt solution would be less than that measured in water. The reverse would be true if the ratio were less than unity.

It is now appropriate to define delta pH (henceforth referred to as $\triangle$pH) by the relation

$\triangle$pH = pH (salt solution) - pH (water), or

$\triangle$pH = pH (high electrolyte conc.) - pH (low electrolyte conc.)

$\triangle$pH's can take on negative or positive values. A negative value indicates that the system is a cation exchanger or at least possesses a net negative charge. A positive value, on the other hand, indicates that the material is an anion exchanger or possesses a net positive charge.

$\triangle$pH for several soils are presented in Tables IV and VI. In general, the Hydrol Humic Latosols (hydrandepts) have the largest

TABLE IV. △pH OF SELECTED HAWAIIAN SOILS.

Soil	Depth (inches)	pH H_2O	pH KCl	△pH KCl-H_2O	pH K_2SO_4	△pH K_2SO_4-H_2O
Akaka (I)	0-8	4.08	4.18	+0.10	4.70	+0.62
	8-16	5.78	5.68	-0.10	6.25	+0.47
	16-24	5.88	5.70	-0.18	6.30	+0.42
	24-30	6.03	5.96	-0.07	6.55	+0.52
	30-38	5.87	5.75	-0.12	6.37	+0.50
	38-54	5.90	5.82	-0.08	6.43	+0.53
	54-59	6.05	5.90	-0.15	6.48	+0.43
	59-63	5.97	5.90	-0.07	6.51	+0.54
	63-73	5.83	5.78	-0.05	6.50	+0.67
Hilo (I)	0-10	4.50	4.70	+0.20	5.34	+0.84
	10-20	5.40	5.40	0.00	6.07	+0.67
	20-30	6.20	6.05	-0.15	6.66	+0.46
	30-42	6.40	6.30	-0.10	6.97	+0.57
Waimea (I)	0-7	5.75	5.47	-0.28	5.97	+0.22
	7-18	5.70	5.35	-0.35	5.82	+0.12
	18-30	5.78	5.40	-0.38	5.92	+0.14
	30-40	5.80	5.40	-0.40	5.85	+0.05
Pahala	0-7	6.30	5.70	-0.60	6.22	-0.08
	7-15	6.30	5.40	-0.90	5.97	-0.33
	15-27	6.70	5.90	-0.80	6.50	-0.20
Waikaloa (I)	0-6	6.30	5.55	-0.75	6.10	-0.20
	6-13	6.60	5.55	-1.05	6.13	-0.47
	13-22	7.05	5.85	-1.20	6.45	-0.60
	22-38	7.38	6.20	-1.18	6.68	-0.70
	38-51	7.70	6.83	-0.87	7.22	-0.48
	51-76	8.23	7.48	-0.75	7.88	-0.35
Paaloa	0-8	4.30	3.90	-0.40	4.32	+0.02
	8-18	4.45	4.00	-0.45	4.50	+0.05
	18-30	4.84	4.10	-0.74	4.68	-0.16
	30-48	4.85	4.11	-0.74	4.70	-0.15

TABLE IV. △pH OF SELECTED HAWAIIAN SOILS. (Continued)

Soil	Depth (inches)	pH H_2O	pH KCl	△pH KCl-H_2O	pH K_2SO_4	△pH K_2SO_4-H_2O
Kolekole	0-7	5.17	4.50	-0.67	4.94	-0.23
	7-16	5.30	4.50	-0.80	4.94	-0.36
	16-34	4.84	4.40	-0.44	4.91	+0.07
	34-50	5.00	4.60	-0.40	5.06	+0.06
	50-66	4.30	3.82	-0.48	4.32	+0.02
Wahiawa	0-5	5.08	4.43	-0.65	4.82	-0.26
	5-18	4.82	4.23	-0.41	4.63	-0.19
	18-30	4.70	4.05	-0.65	4.48	-0.22
Molokai	0-8	6.23	5.48	-0.75	5.95	-0.28
	8-16	6.28	5.48	-0.80	5.96	-0.32
	16-30	5.80	5.30	-0.50	5.88	-0.08
	30-48	6.56	6.22	-0.34	6.75	+0.19
Lualualei	0-6	7.42	6.63	-0.79	7.27	-0.15
	16-18	7.80	6.80	-1.00	7.47	-0.33
	48-60	7.95	7.15	-0.80	7.62	-0.33

number of ΔpH values which are positive or near zero. Potassium sulfate consistently gives higher ΔpH values.

The analogy of anion exchangers used earlier to describe ΔpH cannot be applied to soil in general. If it does apply it would do so in soil containing minerals such as montmorillonite or zeolytes which possess permanent charge. Figure 5 can be used to illustrate this point more effectively.

Figure 5 shows that measurement of pH in 0.01M KNO_3 and 1M KNO_3 solution results in different values. In montmorillonite the pH is always higher in the more dilute solution but in iron oxide the pH becomes more alkaline or more acid depending on the net charge.

Chao et al. (1965) measured pH as a function of electrolyte concentration for a number of sulfate retentive soils. In no case did pH increase with increasing salt concentration when the electrolyte was KCl. Their data suggest that in all cases their soils were near or on the alkaline side of the ZPC. In a number of soils however, pH did increase when the electrolyte was K_2SO_4.

Their data are in line with those of Hingston et al. (1967, 1968) and Atkinson et al. (1967) who suggest that chloride ions are non-specifically adsorbed (indifferent electrolyte) and can replace OH^- in the diffuse double layer, whereas $SO_4^=$ or specifically adsorbed anions can replace OH coordinated to the oxide metal ion. Anions which are specifically adsorbed increase pH even when the pH is greater than the zero point of charge. Rollinson (1956) described this feature of hydrous oxide as follows:

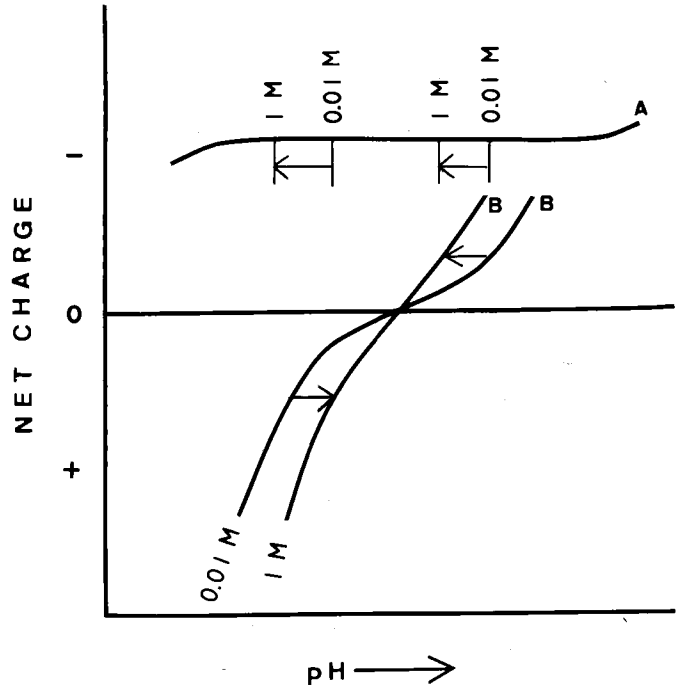

FIGURE 5. EFFECT OF ELECTROLYTE (KNO_3) CONCENTRATION ON pH OF MONTMORILLONITE (A) AND IRON OXIDE (B).

> The addition of solutions of neutral salts to aluminum oxide sols increased the pH of the sols in all cases. This was evidently not due to dilution, since there was practically no effect on the pH when water was added in quantities equal to the volume of the salt solutions used. The magnitude of the effect depended on the salt added. This phenomenon may be explained by anion penetration, since displacement of a hydroxo or an ol group by an anion would increase the pH of the hydrosol.
>
> The increase in pH accompanying the addition of a given amount of a particular salt was much less if the sol was heated before the salt was added. Heating may have converted many of the ol groups to oxo groups which are much less reactive and more difficult to replace. Since ol groups are less reactive than hydroxo groups, the effect may be partially due to increased olation caused by heating the sols.
>
> The order of decreasing tendency of anions to penetrate into the complex was found to be approximately the same for aluminum oxide, chromium oxide and thorium oxide sols, the order indicating the order of ability of the anions to coordinate.

If one is to determine net surface charge, pH must be measured with an indifferent electrolyte. KCl, KNO_3 or NH_4ClO_4 are appropriate salts since the anions do not enter into coordination with iron oxide.

Delta pH measured with an indifferent electrolyte can also be explained on the basis of double layer theory. In double layer theory the relationship between surface potential ψ and the net volume charge density ρ as a function of distance X away from the charged surface is described by Poisson's equation

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi\rho}{D} \qquad (1)$$

where D is the dielectric constant of water. The density ρ is related to the difference between the number of positive and negative ions per unit volume by the expression

$$\rho = -2 z e \eta_0 \text{ Sinh } \frac{z e \psi}{k T} \qquad (2)$$

where z is the ion valence, e is the electrostatic unit, η_0 is the concentration of the ion species in the bulk solution, k is the Boltzmann constant and T is absolute temperature. If equation (2) is combined with equation (1) and solved for $\frac{z e \psi_0}{k T} \ll 1$, and the following boundary condition

$$\left.\begin{array}{l} \psi = \psi_0 \quad X = 0 \\ X \longrightarrow 0 \\ \frac{d\psi}{dX} \longrightarrow 0 \end{array}\right\} \quad X \longrightarrow \infty$$

the solution takes the form

$$\psi = \psi_0 \; e^{-k X}$$

where

$$K = \sqrt{\frac{8\pi e^2 \eta_0 z^2}{D k T}}$$

and ψ_0 is the potential at the surface.

If the surface charge σ is equated to the net space charge by the expression

$$\sigma = - \int_0^\infty \rho \, dX$$

One can obtain for low potentials the relation

$$\sigma = \frac{D K}{4\pi} \psi_0 \qquad (3)$$

For a symmetrical electrolyte such as KCl, KNO_3 or $KClO_4$, K varies with the electrolyte concentration C at 25°C by the relation

$$K = 0.33 \times 10^8 Z \sqrt{C}$$

Depending on the kind of colloid surface, altering K by changing the electrolyte concentration results in a change in the surface charge σ, surface potential ψ or both. Oxide surfaces can be considered to be constant potential surfaces so long as the concentration of the potential determining ions is held constant.

In ΔpH measurements the pH of a sample is measured in water (low K) and one molar solution (high K). If a pH difference (ΔpH) is obtained this means that the concentration of the potential determining ion has changed so that both surface potential and surface charge must have changed. The only significance of ΔpH values is that a negative quantity implies a net negative charge, whereas a positive quantity indicates that the surfaces possesses a net positive charge.

When a positive ΔpH is obtained with K_2SO_4, the significance of this value is quite different. It does not necessarily indicate that the surface is positively charged, for sulfate ion can displace coordinated hydroxols even when an oxide surface possesses a net negative charge.

From a purely practical standpoint ΔpH values obtained by K_2SO_4 might be more useful. It is in a sense related to the anion adsorptive capacity of a soil.

Exchange between hydroxo groups coordinated to oxide metal ions and anions in solution depends on the anion species. Since phosphate

anion is strongly adsorbed by ferruginous soils, one can expect positive ΔpH's with salts containing this anion. Data for Hilo and Akaka soils are presented in Table V. Although KH_2PO_4 solutions have pH values between 4.50 and 5.18, depending upon concentration, and possesses buffering capacity, addition of this salt results in some increases in pH indicating clear evidence for ligand exchange. When KCl was the salt both soils gave negative ΔpH values.

There was reason to believe that ΔpH values vary with time of storage and drying. Kanehiro and Sherman (1956), for example, have shown that cation exchange capacities of certain Hawaiian soils decrease with dehydration. Since ΔpH is, in one sense, related to the difference between anion exchange capacity and cation exchange capacity (net charge) any change in these parameters should be reflected in ΔpH values. Tables VI and VIII show the effect of storage time and drying on pH values.

Unexpectedly, drying appears to have little effect on ΔpH. Samples used in this study were selected to represent those that would suffer severe reduction in cation exchange capacities upon drying. The relatively stable ΔpH values suggest that charge reversal did not occur even with severe drying or long storage.

Since ΔpH values are small and subject to the combined errors of pH measurement in water and salt solution, one cannot take seriously variations in ΔpH units of less than 0.05.

B. Anion adsorption isotherms

1. Sulfate adsorption

Anion adsorption by a particular sample depends upon the pH and anion concentration of the equilibrium solution and also

TABLE V. CHANGE IN pH BY ADDING KH_2PO_4.

$PO_4^{\equiv}$ Added me/2.5 g O.D. Soil	pH (Paste)
	HILO (I-4) SOIL
0.00	6.50
0.25	6.71
0.50	6.82
0.75	6.80
1.25	6.74
1.75	6.63
2.50	6.50
5.00	6.30
7.50	--
	AKAKA (I-5) SOIL
0.00	5.87
0.25	6.13
0.50	6.23
0.75	--
1.00	6.23
1.25	--
1.50	6.20
1.75	--
2.50	6.10
3.50	6.00
5.00	5.90
7.50	--
10.00	5.90

TABLE VI. EFFECT OF STORAGE TIME ON △pH.

Soil	Depth (inches)	pH H_2O	pH KCl	△pH KCl-H_2O	pH K_2SO_4	△pH K_2SO_4-H_2O
			FRESH SOIL (DECEMBER 8, 1968)			
Akaka (II)	0-6	5.28	5.00	-0.28	5.53	+0.25
	6-12	5.37	5.38	+0.01	5.89	+0.52
	40-48	5.87	5.80	-0.07	6.36	+0.49
	55-60	6.10	6.04	-0.06	6.48	+0.38
	64-70	5.92	5.90	-0.02	6.40	+0.48
	78-85	5.97	6.00	+0.03	6.50	+0.53
	85-95	5.87	5.85	-0.02	6.37	+0.50
Hilo (II)	0-8	4.67	4.79	+0.12	5.30	+0.63
	20-32	6.57	6.32	-0.25	6.87	+0.30
Honokaa	0-6	5.60	5.20	-0.40	5.71	+0.11
	8-16	6.25	5.91	-0.34	6.45	+0.2
	16-30	6.52	6.26	-0.26	6.76	+0.24
	30-36	6.39	6.12	-0.27	6.62	+0.23
Waimea (II)	0-8	6.82	5.90	-0.92	6.44	-0.38
	8-16	7.03	6.14	-0.89	6.69	-0.34
	16-25	7.10	6.37	-0.73	6.92	-0.18
Waikaloa (II)	0-10	7.37	6.15	-1.22	6.57	-0.80
	10-16	7.41	6.50	-0.91	6.90	-0.51
	16-26	7.75	7.05	-0.70	7.34	-0.41
Kawaihae	0-8	7.19	6.35	-0.84	6.81	-0.38
	8-16	7.48	6.95	-0.53	7.37	-0.11
	16-24	8.10	7.42	-0.68	7.82	-0.28

TABLE VI. EFFECT OF STORAGE TIME ON △pH. (Continued)

Soil	Depth (inches)	pH H_2O	pH KCl	△pH KCl-H_2O	pH K_2SO_4	△pH K_2SO_4-H_2O
		AFTER 1 MONTH (JANUARY 13, 1969)				
Akaka (II)	0-6	5.33	5.05	-0.28	5.55	+0.22
	6-12	5.42	5.42	0.00	5.91	+0.49
	40-48	5.94	5.90	-0.04	6.42	+0.48
	55-60	6.16	6.16	0.00	6.56	+0.40
	64-70	5.99	5.99	0.00	6.48	+0.49
	78-85	6.10	6.13	+0.03	6.58	+0.48
	85-95	6.00	5.95	-0.05	6.42	+0.42
Hilo (II)	0-8	4.70	4.80	+0.10	5.29	+0.59
	20-32	6.65	6.42	-0.23	6.94	+0.29
Honokaa	0-6	5.60	5.22	-0.38	5.71	+0.11
	8-16	6.28	5.96	-0.32	6.49	+0.21
	16-30	6.58	6.30	-0.28	6.80	+0.22
	30-36	6.40	6.20	-0.20	6.68	+0.28
Waimea (II)	0-8	6.91	5.92	-0.99	6.44	-0.47
	8-16	7.12	6.17	-0.95	6.71	-0.41
	16-25	7.24	6.40	-0.84	6.92	-0.32
Waikaloa (II)	0-10	7.25	6.17	-1.08	6.60	-0.65
	10-16	7.43	6.53	-0.90	6.96	-0.47
	16-26	7.81	7.10	-0.71	7.45	-0.36
Kawaihae	0-8	7.12	6.44	-0.68	6.87	-0.25
	8-16	7.56	7.00	-0.56	7.42	-0.14
	16-24	8.12	7.50	-0.62	7.89	-0.23

TABLE VI. EFFECT OF STORAGE TIME ON ΔpH. (Continued)

Soil	Depth (inches)	pH H_2O	pH KCl	ΔpH KCl-H_2O	pH K_2SO_4	ΔpH K_2SO_4-H_2O
		AFTER 6 MONTHS (JUNE 8, 1969)				
Akaka (II)	0-6	5.10	4.98	-0.12	5.53	+0.43
	6-12	5.39	5.35	-0.04	5.90	+0.51
	40-48	5.93	5.81	-0.12	6.40	+0.47
	55-60	6.10	6.04	-0.06	6.50	+0.40
	64-70	6.00	5.94	-0.06	6.48	+0.48
	78-85	6.00	6.04	+0.04	6.52	+0.52
	85-95	6.00	5.90	-0.10	6.43	+0.43
Hilo (II)	0-8	4.59	4.72	+0.13	5.25	+0.66
	20-32	6.65	6.38	-0.27	6.95	+0.30
Honokaa	0-6	5.45	5.13	-0.32	5.75	+0.25
	8-16	6.28	5.90	-0.38	6.48	+0.20
	16-30	6.59	6.29	-0.30	--	--
	30-36	6.41	6.18	-0.23	--	--
Waimea (II)	0-8	6.82	5.81	-1.01	6.34	-0.48
	8-16	7.16	6.08	-1.08	6.63	-0.53
	16-25	7.30	6.31	-0.99	6.87	-0.43
Waikaloa (II)	0-10	7.00	6.01	-0.99	6.47	-0.53
	10-16	7.50	6.40	-1.10	6.85	-0.65
	16-26	7.83	7.00	-0.83	7.34	-0.49
Kawaihae	0-8	7.10	6.35	-0.75	6.77	-0.33
	8-16	7.50	6.90	-0.60	7.30	-0.20
	16-24	8.02	7.35	-0.67	7.75	-0.27

TABLE VII. EFFECT OF DRYING ON △pH.

Soil	Depth (inches)	Percent Moisture	pH H_2O	pH K_2SO_4	△pH
		NO DRYING (DECEMBER 8, 1968)			
Akaka (I)	30-38	414.0	5.87	6.37	+0.50
	63-73	481.0	5.83	6.50	+0.67
Akaka (II)	0-6	86.6	5.28	5.53	+0.25
	40-48	341.0	5.85	6.36	+0.49
	64-70	419.0	5.92	6.40	+0.48
	85-95	348.0	5.87	6.37	+0.50
Akaka (III)	0-6	--	--	--	--
Hilo (I)	0-10	64.6	4.50	5.34	+0.84
	10-20	90.4	5.40	6.07	+0.67
	30-42	205.0	6.40	6.97	+0.57
Hilo (II)	0-8	66.6	4.67	5.30	+0.63
	20-32	253.0	6.57	6.87	+0.30
		1 DAY OF DRYING (DECEMBER 10, 1968)			
Akaka (I)	30-38	340.0	5.90	6.40	+0.50
	63-73	345.0	5.90	6.51	+0.61
Akaka (II)	0-6	43.1	5.22	5.56	+0.34
	40-48	219.0	5.92	6.42	+0.50
	64-70	311.0	5.98	6.47	+0.49
	85-95	263.0	5.87	6.42	+0.55
Akaka (III)	0-6	119.0	3.80	4.30	+0.5
Hilo (I)	0-10	31.0	4.60	5.40	+0.8
	10-20	37.7	5.30	5.97	+0.67
	30-42	124.0	6.50	6.93	+0.43
Hilo (II)	0-8	35.0	4.68	5.30	+0.62
	20-32	184.0	6.67	6.94	+0.27

TABLE VII. EFFECT OF DRYING ON △pH. (Continued)

Soil	Depth (inches)	Percent Moisture	pH H_2O	pH K_2SO_4	△pH
		2 DAYS OF DRYING (DECEMBER 11, 1968)			
Akaka (I)	30-38	228.0	5.94	6.43	+0.49
	63-73	141.0	5.90	--	--
Akaka (II)	0-6	19.6	5.48	5.63	+0.15
	40-48	83.2	--	--	--
	64-70	193.0	6.07	6.52	+0.45
	85-95	149.0	6.03	6.50	+0.47
Akaka (III)	0-6	75.4	3.83	4.32	+0.49
Hilo (I)	0-10	18.3	4.64	5.42	+0.78
	10-20	18.4	5.32	5.97	+0.65
	30-42	40.3	5.80	6.52	--
Hilo (II)	0-8	16.8	4.70	5.33	+0.63
	20-32	94.5	6.70	6.95	+0.26
		5 DAYS OF DRYING (DECEMBER 14, 1968)			
Akaka (I)	30-38	34.4	5.6	6.40	+0.80
	63-73	41.9	5.58	6.50	+0.92
Akaka (II)	0-6	--	5.57	5.68	+0.11
	40-48	22.6	5.54	6.37	+0.83
	64-70	28.7	5.80	6.48	+0.68
	85-95	22.8	5.70	6.43	+0.73
Akaka (III)	0-6	16.4	3.90	4.41	+0.51
Hilo (I)	0-10	16.2	4.64	5.46	+0.82
	10-20	19.2	5.35	5.98	+0.62
	30-42	22.1	5.77	6.82	+1.05
Hilo (II)	0-8	15.7	4.77	5.37	+0.60
	20-32	23.0	6.05	6.82	+0.77

TABLE VII. EFFECT OF DRYING ON ΔpH. (Continued)

Soil	Depth (inches)	Percent Moisture	pH H_2O	pH K_2SO_4	ΔpH
		15 DAYS OF DRYING (DECEMBER 24, 1968)			
Akaka (I)	30-38	26.1	5.57	6.30	+0.73
	63-73	26.5	5.54	6.40	+0.86
Akaka (II)	0-6	16.3	5.47	5.67	+0.20
	40-48	20.8	5.44	6.30	+0.86
	64-70	26.2	5.62	6.40	+0.78
	85-95	21.7	5.52	6.34	+0.82
Akaka (III)	0-6	12.1	3.88	4.38	+0.50
Hilo (I)	0-10	15.1	4.64	5.44	+0.80
	10-20	16.1	5.31	5.94	+0.63
	30-42	20.6	5.80	6.75	+0.95
Hilo (II)	0-8	14.4	4.77	5.35	+0.58
	20-32	20.5	6.00	6.77	+0.77

on the anion species. Adsorption theory is much simplified when for a given pH and ion species, maximum adsorption occurs at some finite solution concentration. Evidence for the existence of maximum anion adsorption in soil materials is scanty at best. However maximum adsorption has been reported on a few soils, kaolinite and oxide samples, and these are summarized in Table VIII.

Maximum adsorption in Hawaiian soils is particularly difficult to demonstrate because of their high anion adsorptive capacity. This is especially true with phosphate adsorption at pH less than 7.

In the case of sulfate adsorption, adsorption maxima for most Hawaiian soils are ill-defined owing to the fact that most samples contain high amounts of native sulfate. In special cases the native sulfate content is low so that a reasonable isotherm displaying a well-defined maximum can be obtained. This was the case with the 50 to 66 inch depth horizon of the Kolekole profile as shown in Figure 6. When a well-defined maximum is obtained, adsorption can be described by the Langmuir adsorption equation as shown in Figure 7.

In most cases maximum sulfate adsorption is much increased by washing the sample with 2N KCl solution. Figures 8, 9 and 10 show the effects of KCl-washing or KCl-washing plus dialysis on sulfate adsorption for the Wahiawa, Hilo and Akaka samples. Adsorption on a KCl-washed, dialyzed sample is consistently lower than the sample receiving KCl-washing

TABLE VIII. SOME REPORTED CASES OF MAXIMUM ANION ADSORPTION.

Source	Anion	pH	Adsorbent
Kamprath et al. (1956)	Sulfate	4.0, 5.0	Cecil soil
Aylmore et al. (1966)	Sulfate	4.6	Iron oxide, aluminum oxide, API-9 Kaolin, Clackline, Kaolin
Muldjadi et al. (1966)	Phosphate	3-10	Kaolinite, Gibbsite, Pseudoboehmite
Hingston et al. (1968)	Pyrophosphate	--	Goethite

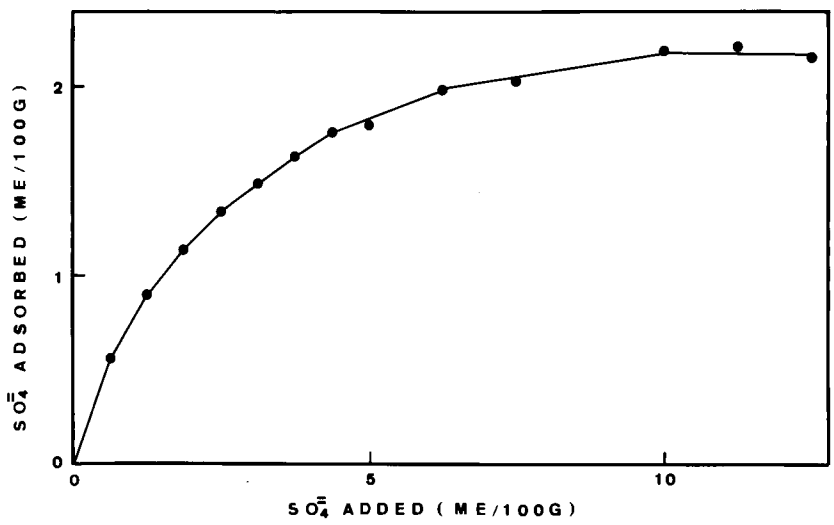

FIGURE 6. SULFATE ADSORPTION ISOTHERM FOR AN UNTREATED KOLEKOLE (5) SOIL. THE SOIL TO SOLUTION RATIO WAS 1:2.6.

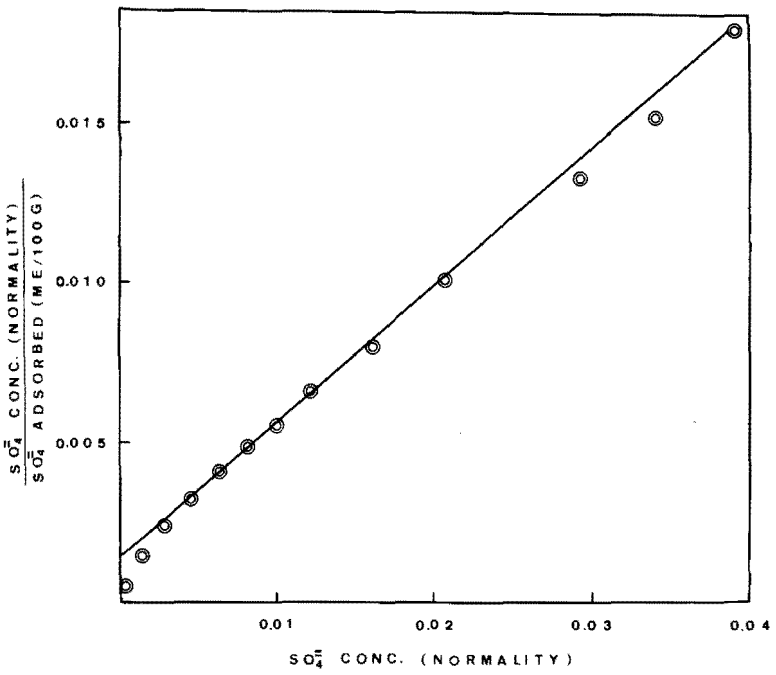

FIGURE 7. LANGMUIR PLOT OF SULFATE ADSORPTION ISOTHERM FOR UNTREATED KOLEKOLE (5) SOIL. THE SOIL TO SOLUTION RATIO WAS 1:2.6.

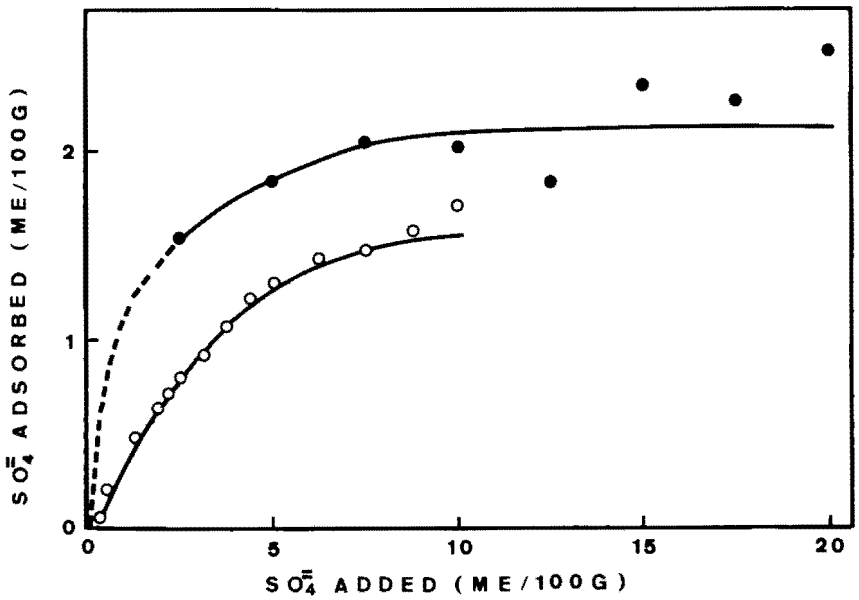

FIGURE 8. SULFATE ADSORPTION ISOTHERMS FOR AN UNTREATED (O) AND KC1-WASHED (●) WAHIAWA (3) SOIL. THE SOIL TO SOLUTION RATIOS FOR THE UNTREATED AND KC1-WASHED SAMPLES WERE 1:2.6 AND 1:3.8, RESPECTIVELY.

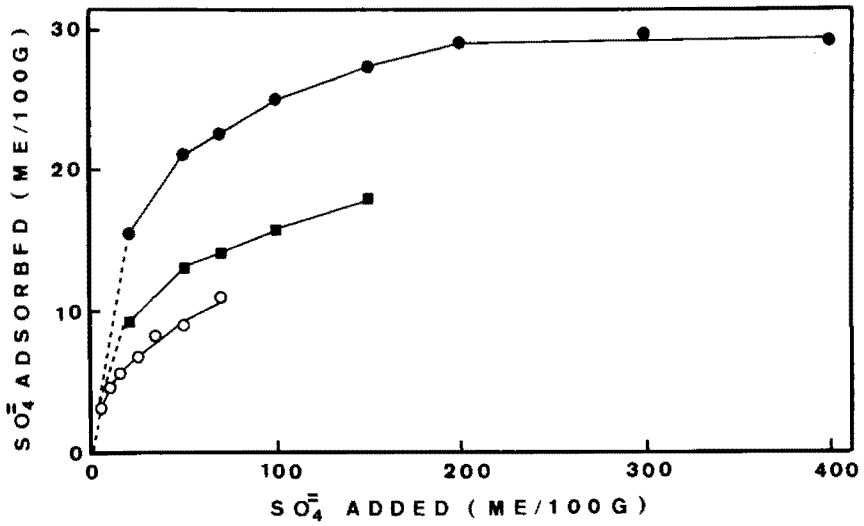

FIGURE 9. SULFATE ADSORPTION ISOTHERMS FOR AN UNTREATED (O), KCl-WASHED AND DIALYZED (■) AND KCl-WASHED (●) HILO (I-4) SOIL. THE SOIL TO SOLUTION RATIOS FOR THE UNTREATED, DIALYZED AND KCl-WASHED SAMPLES WERE 1:12, 1:12 AND 1:14, RESPECTIVELY.

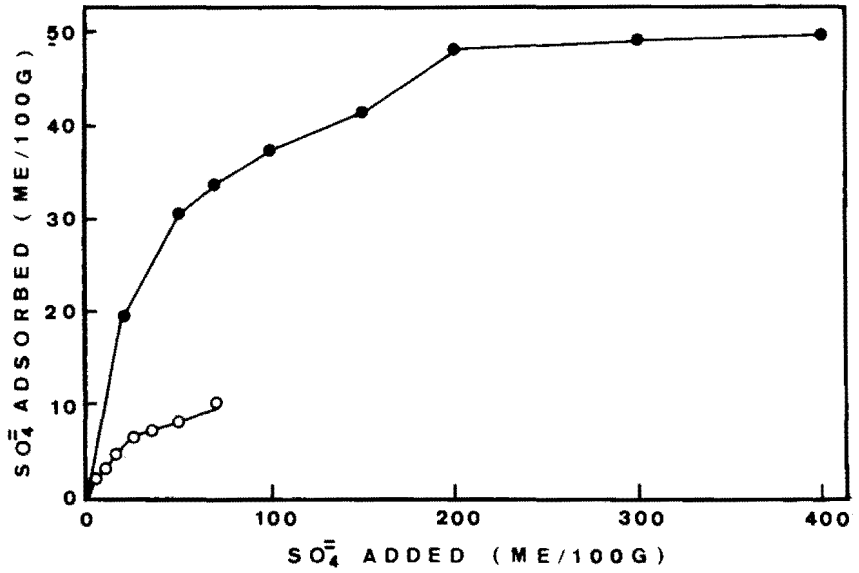

FIGURE 10. SULFATE ADSORPTION ISOTHERMS FOR AN UNTREATED (O) AND KCl-WASHED (●) AKAKA (I-5) SOIL. THE SOIL TO SOLUTION RATIOS FOR THE UNTREATED AND KCl-WASHED SAMPLES WERE 1:14 AND 1:15, RESPECTIVELY.

alone. Dialysis appears to disperse organic matter and the author believes that adsorption of organic matter reduces sulfate adsorption. This point however was not studied further and remains essentially unproven.

Sulfate adsorption in several samples showed double maxima. These appeared consistently in high sulfate retentive samples such as in the Akaka soils. Figures 11 and 12 show the adsorption isotherm plotted in the conventional manner and in the Langmuir form, respectively. Aylmore et al. (1965) showed a similar sulfate adsorption pattern on kaolinite.

2. Nitrate adsorption

Nitrate adsorption on untreated soil samples is relatively small and generally less than 2 or 3 me per 100 grams. In most soils nitrate adsorption is negligibly small. Nitrate adsorption however can be increased to significant levels by removing native sulfate.

Figures 13 and 14 show nitrate adsorption for a KCl-washed and KCl-washed plus dialyzed sample of the Hilo and Akaka samples, respectively. Dialysis reduces nitrate adsorption as was the case with sulfate adsorption.

According to Parks and de Bruyn nitrate ions are not specifically adsorbed but are retained as counter ions opposite a positively charged surface. Anions which are adsorbed as counter ions are easily leached, and the adsorption capacity is highly pH dependent. Furthermore, adsorption of

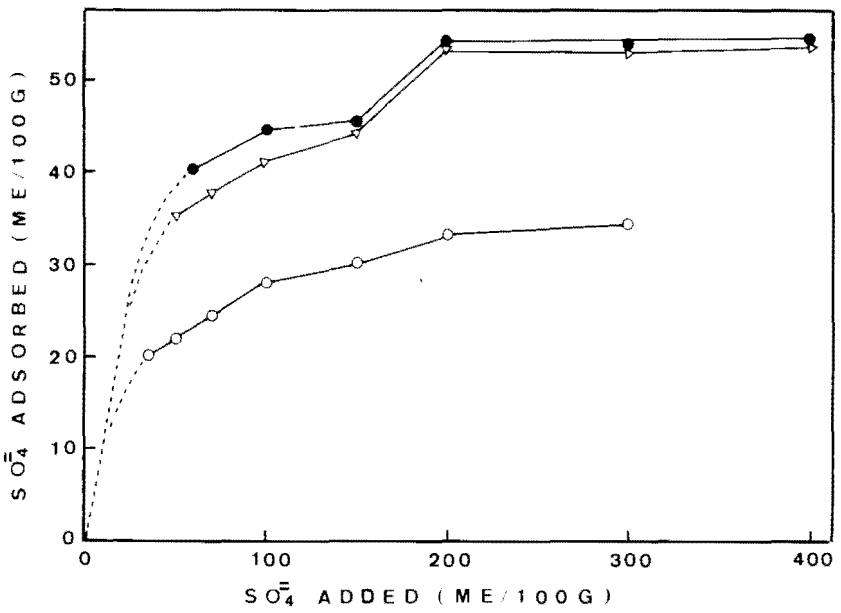

FIGURE 11. SULFATE ADSORPTION ISOTHERMS FOR KCl-WASHED HONOKAA (O), AKAKA (II-5) ( ) AND AKAKA (I-9) (●) SOILS. THE SOIL TO SOLUTION RATIOS FOR THE HONOKAA, AKAKA (II-5) AND AKAKA (I-9) SAMPLES WERE 1:14, 1:15 AND 1:16, RESPECTIVELY.

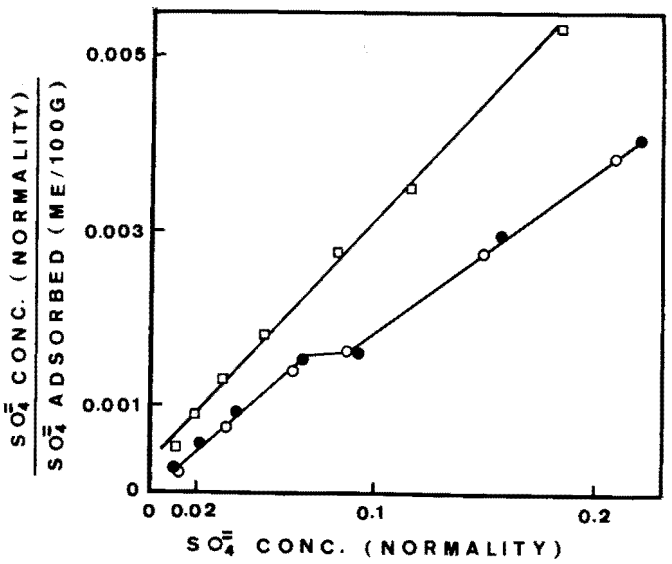

FIGURE 12. LANGMUIR PLOTS OF SULFATE ADSORPTION ISOTHERM FOR KCl-WASHED HONOKAA (□), AKAKA (II-5) (●) AND AKAKA (I-9) (O) SOILS. THE SOIL TO SOLUTION RATIOS OF THE HONOKAA, AKAKA (II-5) AND AKAKA (I-9) WERE 1:14, 1:15 AND 1:16, RESPECTIVELY.

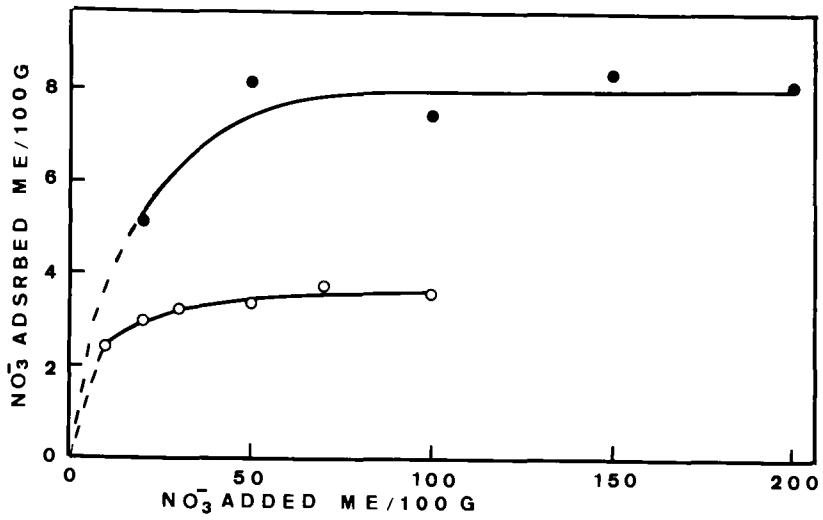

FIGURE 13. NITRATE ADSORPTION ISOTHERMS FOR KCl-WASHED (●) AND KCl-WASHED AND DIALYZED (O) HILO (I-4) SOIL. THE SOIL TO SOLUTION RATIOS FOR THE KCl-WASHED AND DIALYZED SAMPLES WERE 1:14 AND 1:12, RESPECTIVELY.

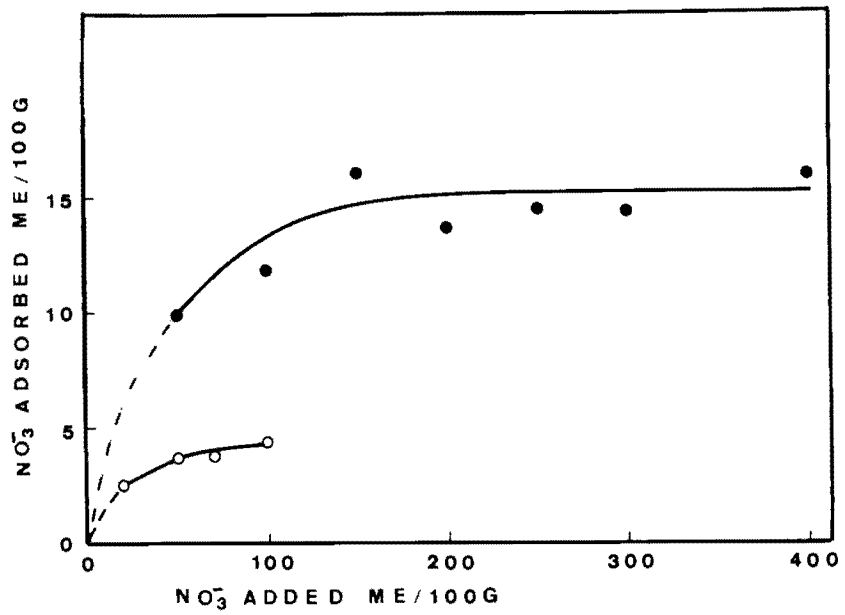

FIGURE 14. NITRATE ADSORPTION ISOTHERMS FOR KCl-WASHED (●) KCl-WASHED AND DIALYZED (O) AKAKA (I-5) SOIL. THE SOIL TO SOLUTION RATIOS FOR THE KCl-WASHED AND DIALYZED SAMPLES WERE 1:16 AND 1:14, RESPECTIVELY.

specifically adsorbed anion such as sulfate has been shown to render a surface more negative (Hingston et al., 1967). The reverse could also be true so that removal of sulfate could render a surface more positive allowing for greater nitrate adsorption.

3. Phosphate adsorption

Phosphate ions are strongly adsorbed by ferruginous soils. Phosphate adsorption is also strongly influenced by soil pH, with more phosphorus being adsorbed in acid range. Figures 15 and 16 illustrate the effect of concentration and type of salt on phosphate adsorption for Wahiawa (3) and Hilo (I-4) soils, respectively. In the case of the alkaline salt ($Na_3PO_4 \cdot 12H_2O$) maximum adsorption was easily attained. This was not true for acid ($NaH_2PO_4 \cdot H_2O$) salt. Increasing phosphorus adsorption with increasing concentration of the acid salt was a function not only of concentration but also a function of decreasing pH. As the concentration of the acid salt was increased the pH of the equilibrating solution was lowered and it becomes difficult to differentiate between pH and concentration effects on phosphorus adsorption.

In Figure 17, the same data presented in Figure 16, phosphorus is plotted as a function of pH for a number of concentrations. In this form the data bear out the earlier trend of higher phosphorus adsorption in acid medium.

Since the form of phosphate adsorbed by the soil is not known it is not proper to express adsorption as me/100 gms for in this form $PO_4^{\equiv}$ ion would satisfy three times the number

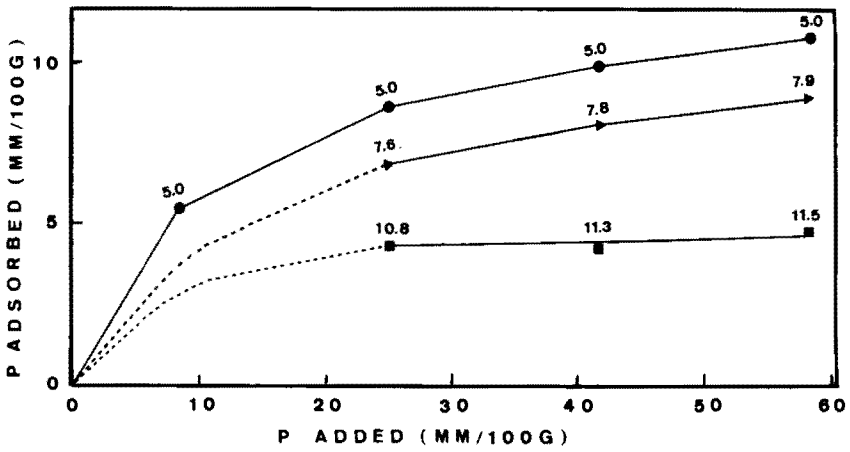

FIGURE 15. PHOSPHATE ADSORPTION ISOTHERMS FOR A WAHIAWA (3) SOIL AS A FUNCTION OF CONCENTRATION AND pH USING $NaH_2PO_4 \cdot H_2O$ (●), $Na_2HPO_4 \cdot 7H_2O$ (▲) AND $Na_3PO_4 \cdot 12H_2O$ (■). THE SOIL TO SOLUTION RATIO WAS 1:2.6. THE NUMBERS OVER THE EXPERIMENTAL POINTS REFER TO THEIR EQUILIBRIUM pH. SAMPLES WERE EQUILIBRATED FOR 12 HOURS.

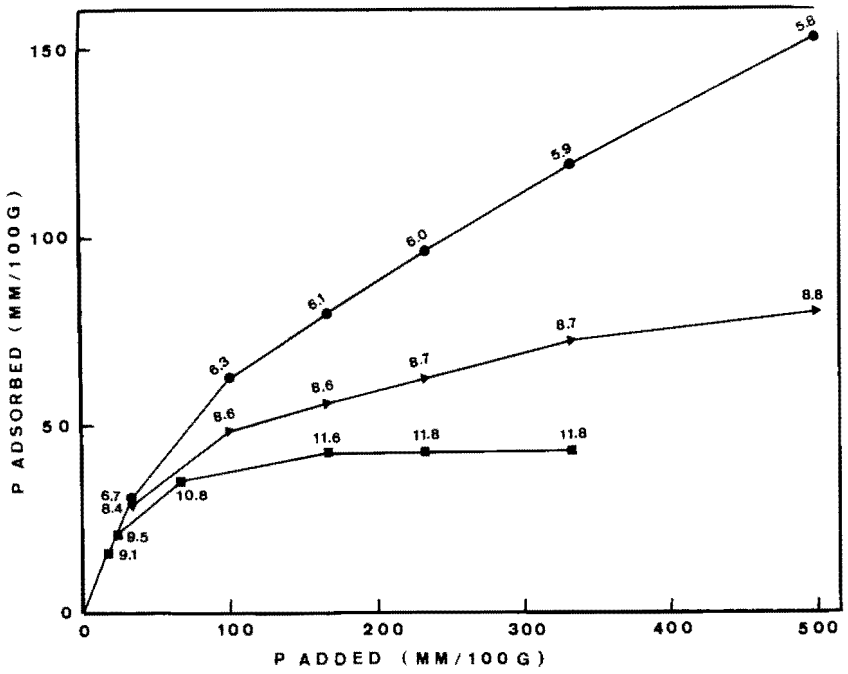

FIGURE 16. PHOSPHATE ADSORPTION ISOTHERMS FOR A HILO (I-4) SOIL AS A FUNCTION OF CONCENTRATION AND pH USING $NaH_2PO_4 \cdot H_2O$ (●), $Na_2HPO_4 \cdot 7H_2O$ (▲) AND $Na_3PO_4 \cdot 12H_2O$ (■). THE SOIL TO SOLUTION RATIO WAS 1:12. THE NUMBERS OVER THE EXPERIMENTAL POINTS REFER TO THEIR EQUILIBRIUM pH. SAMPLES WERE EQUILIBRATED FOR 12 HOURS.

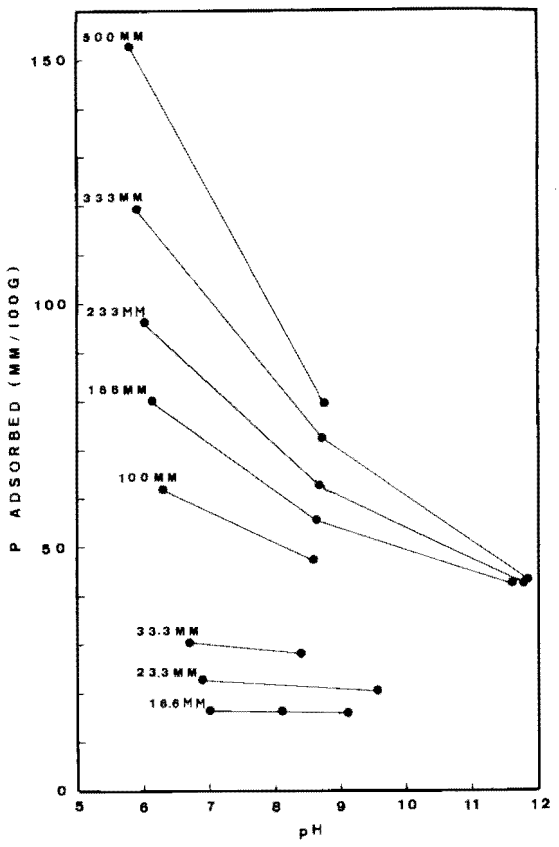

FIGURE 17. EFFECT OF pH ON PHOSPHATE ADSORPTION BY A HILO (I-4) SOIL FOR VARIOUS CONCENTRATIONS. THE ISO-CONCENTRATION CURVES REPRESENT MILLIMOLE OF PHOSPHATE ADDED PER 100 G. THE SOIL TO SOLUTION RATIO WAS 1:12. SAMPLES WERE EQUILIBRATED FOR 12 HOURS.

of sorption site as $H_2PO_4^-$. For this reason many workers prefer to express adsorbed phosphorus as millimoles per 100 gms.

Phosphate anions are adsorbed specifically and can be adsorbed to a greater extent than sulfate ions. According to Nagarajal et al. (1968) maximum adsorption at any pH is limited by the negative charge that a surface can acquire, and that the limiting value is in turn determined by the nature of the anion. For example, more phosphate is adsorbed than sulfate at a given pH because the phosphate anion has a greater capacity for rendering the surface negative.

There is another important consequence of phosphate adsorption. Adsorption of phosphate shift the zero point of charge to lower pH values. This phenomenon, for example, can render a soil surface more negative by simple phosphate application. A soil with a net positive charge can be altered to one with net negative charge by addition of an appropriate anion. This feature of oxide soil is discussed in a later section.

C. Sulfate adsorption capacities and sulfate content of Hawaiian soils

Using the acetone washing method described in the materials and methods section, sulfate adsorption capacities of 50 samples constituting 11 soil series were determined. These values are presented in Table IX. The sulfate adsorption capacities range in values from less than 1 me/100 gms of oven-dried soil to a high of 84 me/100 gms. Most of the values for anion ($SO_4^=$) exchange or anion adsorption fall below 2 me/100 gms of soil. However, Wada

TABLE IX. SULFATE ADSORPTION CAPACITIES AND SULFATE SATURATION OF SELECTED HAWAIIAN SOILS.

Soil	Depth (inches)	Sulfate Adsorption Capacity (me/100 g)	Sulfate Content (me/100 g)	Sulfate Saturation (%)
Akaka (I)	0-8	18.1	0.0	0.0
	8-16	36.7	22.6	61.5
	16-24	55.7	26.9	48.2
	24-30	50.3	30.0	59.6
	30-38	58.1	34.3	59.0
	38-54	76.7	41.5	54.1
	54-59	41.0	22.0	53.6
	59-63	75.2	41.7	55.4
	63-73	84.0	50.7	60.3
Akaka (II)	0-6	19.0	6.6	34.7
	6-12	69.0	41.7	60.4
	40-48	63.7	37.5	58.8
	55-60	65.5	41.7	63.6
	64-70	74.7	47.0	62.9
	78-85	43.5	31.2	71.7
	85-95	62.5	36.0	57.6
Hilo (I)	0-10	19.5	5.99	30.7
	10-20	16.6	1.33	8.01
	20-30	41.0	15.83	38.5
	30-42	34.0	14.4	42.3
Hilo (II)	0-8	17.8	8.21	46.1
	20-32	53.5	27.5	51.4
Honokaa	0-6	19.0	4.91	25.8
	8-16	36.1	10.7	29.6
	16-30	74.2	22.0	29.6
	30-36	49.2	17.5	35.5
Waimea (II)	0-8	3.56	0.0	0.0
	8-16	3.23	0.0	0.0
	16-25	3.21	0.0	0.0

TABLE IX. SULFATE ADSORPTION CAPACITIES AND SULFATE SATURATION OF SELECTED HAWAIIAN SOILS. (Continued)

Soil	Depth (inches)	Sulfate Adsorption Capacity (me/100 g)	Sulfate Content (me/100 g)	Sulfate Saturation (%)
Waikaloa (II)	0-10	2.5	0.000	0.00
	10-18	2.62	0.023	0.87
	18-26	0.75	0.395	52.6
Kawaihae	0-8	3.37	0.293	8.69
	8-16	3.83	0.81	21.1
	16-24	3.72	1.03	27.6
Paaloa	18-30	3.43	0.652	19.0
	30-48	3.73	1.20	32.1
Kolekole	0-7	0.06	0.000	0.0
	7-16	1.48	0.111	7.5
	16-34	2.96	1.18	39.8
	34-50	3.95	0.752	19.0
	50-66	2.83	0.468	16.5
Wahiawa	0-5	1.31	0.00	0.0
	5-18	2.93	1.04	35.4
	18-30	3.90	1.62	41.5
Molokai	0-8	0.06	0.000	0.00
	8-16	1.60	0.037	2.31
	16-30	2.00	0.996	49.8
	30-48	2.34	0.780	33.3
Lualualei	0-6	0.93	--	--

and Ataka (1958) reported anion (Cl^-) exchange capacities in excess of 80 me/100 gms. Aylmore et al. (1966) reported sulfate adsorption to the extent of 13 to 80 me/100 gms at a pH of 4.6 for synthesized iron and aluminum hydroxides.

Figure 18 shows the relation between native sulfate sulfur content and sulfate adsorption capacity. Other than the highly significant correlation between these two variables, there are a number of interesting features in this relationship. First, there appears to be two populations with respect to sulfate content or sulfate adsorption capacities of Hawaiian soils. The first group includes soil with less than 5 me of adsorption capacities with a mean and standard deviation of 2.53 and 1.20, respectively, and a second group with adsorption capacities greater than 10 me with a mean and standard deviation of 43.3 and 21.5, respectively. The second group consists of horizons from the Akaka, Hilo and Honokaa series, while the first group is comprised of horizons from the remaining series. There is no overlap between groups.

There is reason to believe that the free ion oxide content is not a particularly useful index to estimate the anion adsorption capacity of a soil. It appears that the oxide surface of the Hydrandept (Hydrol Humic Latosols) is much more active than the Oxisols, for example, the Low Humic or Humic Ferruginous Latosols (Haplustoxs). One can make rough comparisons of the oxide activity of both groups. The average Fe_2O_3 content of the Hydrandept is about 40 percent so that the sulfate adsorption

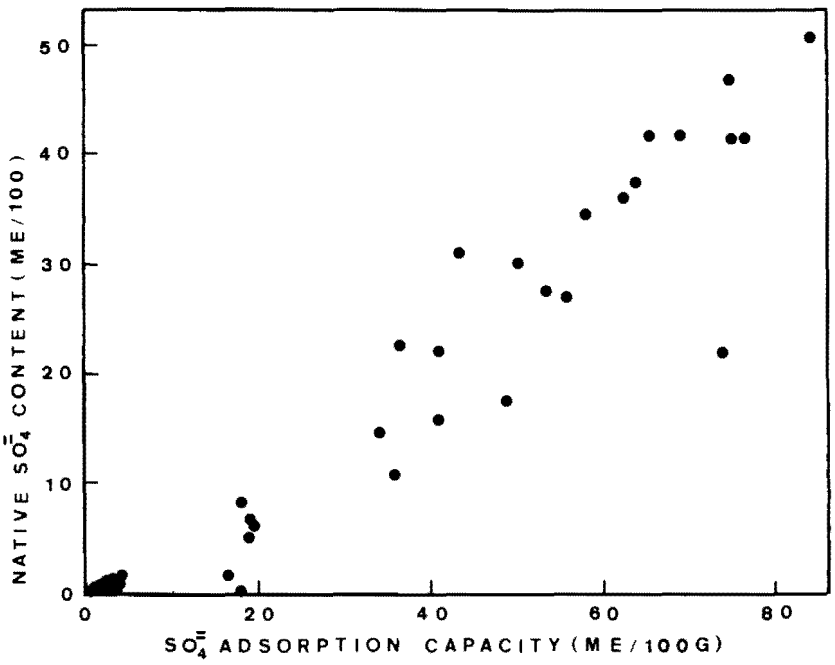

FIGURE 18. THE RELATIONSHIP BETWEEN NATIVE SULFATE SULFUR CONTENT AND SULFATE ADSORPTION CAPACITY.

capacity would be 1 me per gram of oxide for this group. The average Fe_2O_3 content for the remaining group is 25 percent so that the sulfate adsorption capacity would be 0.1 me per gram or ten times lower than the first group. Hydrous oxides of aluminum and non-crystalline, hydrated alumino-silicates may also contribute significantly to anion adsorption. Rollinson (1956, page 470) suggests that reactivity of hydrous oxides is much reduced by aging. His explanation is as follows:

> According to the coordination theory, precipitated hydrous oxides are considered polymeric compounds not different in kind from those existing in crystalloidal solutions and colloidal dispersions. They are regarded as complexes of zero charge produced by a continued process of olation, accompanied or followed by oxalation and perhaps by anion penetration. This point of view furnishes an explanation of two well-known characteristics of hydrous oxides, such as those of aluminum and chromium - their decreased chemical reactivity after aging or heating and their ability to retain certain impurities even after exhaustive washing.
>
> As to the first, to these, a freshly precipitated hydroxide may consist of complexes of relatively low aggregate weight containing a high ratio of ol to oxo groups. For a given weight of hydroxide, the smaller the aggregates, the more "end groups" there will be, i.e., hydroxo and aquo groups. The hydroxo groups are easily convertible to aquo groups by the action of hydrogen ions and may easily be displaced by anions. Ol groups are not so readily attacked by hydrogen ions or displaced by anions but do react slowly. Thus low molecular weight aggregates, which are not too highly oxolated, may be dissolved readily in acid.
>
> However, the process of olation, by which the hydrous oxide was presumably formed, may continue slowly after precipitation, even at low temperature. There is a decrease in the relative number of hydroxo groups, and a corresponding increase in the number of ol and oxo groups. The completely oxolated oxide is quite inert.

Rollinson's explanation seems to describe the oxide in Hawaiian soil with considerable accuracy. The oxides in the Hydrandept are highly hydrated probably due to their high hydroxo, aquo and ol coordination, whereas the soils with low anion adsorption consist mainly of oxo groups. Dehydration and aging could render oxides less reactive.

Lastly the highly hydrated nature of the oxides in the Hydrandept further lends support to the thesis that oxide surfaces are coordinated with hydroxo, ol and aquo groups.

D. Effect of soil phosphorus application on cation exchange capacity

Of all the anionic constituents added to soils in large quantities as fertilizer, filler or amendment, phosphorus is probably the most strongly adsorbed. Rarely does phosphorus occur as the trivalent phosphate ion in soil solution, and one would expect phosphorus to be adsorbed as the divalent ($H_2PO_4^{=}$) or monovalent ($H_2PO_4^{-}$) anion. Since the first, second and third dissociation constants of phosphoric acid are 1.1×10^{-2}, 7.5×10^{-8}, and 4.8×10^{-13}, respectively, one would expect the monovalent anion to be the dominant ion in pH's normally encountered in soils.

If the phosphate ion is involved in ligand exchange as it is now believed, steric factors probably would not allow more than one of the bonding oxygens to coordinate with the metal ion. This would suggest that the two remaining bonding oxygens could then act as cation exchange sites. A number of workers

have actually demonstrated this increase in cation exchange capacity with phosphated soils (Toth, 1937; Davis, 1945, Coleman and Mehlich, 1948).

Table X shows the effect of phosphorus adsorption on cation exchange capacity for the Hilo (I-4) soil. The data reduce to the fact that for every millimole of phosphate adsorbed, cation exchange capacity increases by approximately 0.8 me. This implies that phosphorus adsorption increases the net negative charge of the colloid surface.

Hingston et al. (1967) explains this by stating that adsorbed ions confer a negative charge to the surface by displacing the zero point of charge to lower pH values. This can readily be seen by referring to Figure 4 in the review of literature section. The increase in negative charge can be accounted for when polyvalent anions such as phosphate and silicates (H_4SiO_4) are adsorbed, but this becomes somewhat complicated when monovalent ions such as fluoride effect the same change. This then implies that adsorption of an anion by a surface at a particular pH renders the surface more negative at that pH by displacing the zero point of charge to lower pH, and not necessarily because the adsorbed anion possesses a bonding atom.

The greater the capacity of an anion to confer negative charge to a surface the greater degree to which it will be adsorbed. Unlike cation exchange in montmorillonites which involves exchange of counter ions on a surface of constant charge, anion adsorption on oxide surface involves ligand

TABLE X. INFLUENCE OF PHOSPHATE ADSORPTION ON CATION EXCHANGE CAPACITY OF THE HILO (I-4) SOIL.

Source of Phosphorus	P Adsorbed (m mole/100 g)	CEC at pH 7 (me/100 g)	△CEC (me/100 g)	△CEC / P (m mole)
$NaH_2PO_4 \cdot H_2O$	0.00	26.85	--	--
	16.4	38.31	11.5	0.701
	29.37	50.54	23.69	0.806
	57.86	73.71	46.86	0.809
	74.26	88.03	61.18	0.823
	88.88	98.56	71.71	0.806
	109.6	110.7	83.85	0.765
	139.9	127.6	100.7	0.720
$Na_2HPO_4 \cdot 7H_2O$	16.35	40.09	13.2	0.807
	28.93	51.38	24.53	0.847
	49.33	70.55	43.70	0.885
	56.33	77.07	50.22	0.891
	63.39	72.44	45.59	0.719
	69.86	88.45	61.6	0.881
	77.76	93.92	67.05	0.862
$Na_3PO_4 \cdot 12H_2O$	16.14	41.1	14.3	0.885
	21.68	45.23	18.3	0.848

exchange on a constant potential surface. For these reasons one should not make the mistake of viewing anion exchange in terms of cation exchange models. The only exception to this is NO_3^-, ClO_4^- and possibly Cl^- ions which are normally adsorbed as counter ions in the diffuse double layer.

Table XI shows the effect of pH on the cation exchange values of these phosphated soils. A non-phosphated soil will show a higher cation exchange capacity at high pH if the surface is constant potential type surface. When this surface is phosphated, the net negative charge increases, but this charge is still pH dependent. The data in Table XI suggest that dependence of charge on pH of the non-phosphated surface is not significantly different from its phosphated counterpart.

Ayres and Hagihara (1953) reported higher retention of potassium in Hydrol Humic Latosol when this ion was added as phosphate salt. If adsorbed anions render a surface more negative, one can expect potassium ions to be less subject to leaching when the anion is phosphate than when it is sulfate or chloride. This was exactly the observation of Ayres and Hagihara.

There is also reason to believe that the effect of calcium silicate application on Hawaiian soil is one of surface charge reversal. An interesting corollary to this study is the effect of pH on calcium availability in soils with constant potential type surface. When calcium silicate is added to a soil of this kind, the zero point of charge is displaced to lower pH and at the same time the pH is increased so that the net increase in

TABLE XI. INFLUENCE OF pH ON CEC OF PHOSPHATED SOIL.

Soil	pH	P Adsorbed (m mole/100 g)	CEC of Phosphated Soil (me/100 g)	CEC of Untreated Soil (me/100 g)	△CEC (me/100 g)	△CEC / P (m mole)
Hilo (I-4)	5.37	19.77	31.16	21.22	9.94	0.502
	7.00	22.23	43.63	26.85	16.75	0.753
	8.35	22.48	49.53	30.49	19.01	0.845
Akaka (I-5)	5.36	21.82	51.80	--	--	--
	7.00	22.91	63.76	44.85	18.91	0.825
	8.35	23.00	72.86	--	--	--
Wahiawa (III)	5.35	4.11	12.33	--	--	--
	6.94	4.73	15.34	10.95	4.39	0.928
	8.30	4.30	16.84	--	--	--

negative charge is large. Under these conditions calcium ions are strongly adsorbed. As calcium is removed by leaching or plant uptake, the pH is lowered and consequently the surface becomes more positively charged so that calcium saturation may remain constant even though the absolute calcium content may decrease severalfold. This may account for the relative ease with which calcium is adsorbed by plants even in soil of low calcium saturation.

E. Anion interaction

When more than one anion species compete for adsorption, the anion adsorption process becomes more complicated. Non-specifically adsorbed anions would be expected to have little effect on adsorption of specifically adsorbed anions. Figures 19 and 20 show the effect of chloride ion on sulfate adsorption, and clearly demonstrate that chloride ions have little or no influence on sulfate adsorption.

Chloride however appears to behave identically with nitrate ions so that when both are added to a soil, they are equally adsorbed as indicated by the closeness of the nitrate adsorption data to the non-preference line shown in Figure 21.

On the other hand, nitrate ions are negatively adsorbed in the presence of sulfate ions. This is to be expected from what is now known about specific and non-specific adsorption. Sulfate anions are specifically adsorbed, and when adsorbed, render a surface more negative, resulting in repulsion of non-specifically adsorbed ions.

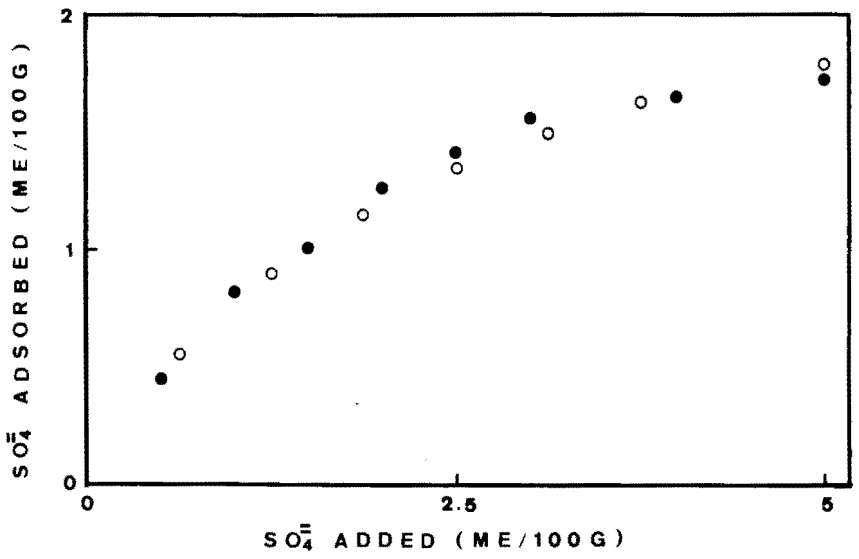

FIGURE 19. EFFECT OF CHLORIDE ON SULFATE ADSORPTION ON KOLEKOLE (5) SOIL. SOLID CIRCLES REPRESENT SULFATE ADSORPTION IN THE ABSENCE OF CHLORIDE. OPEN CIRCLES REPRESENT ADSORPTION IN PRESENCE OF CHLORIDE. THE SUM OF THE SULFATE AND CHLORIDE ION ADDED WAS MAINTAINED AT 5 ME/100 GRAMS.

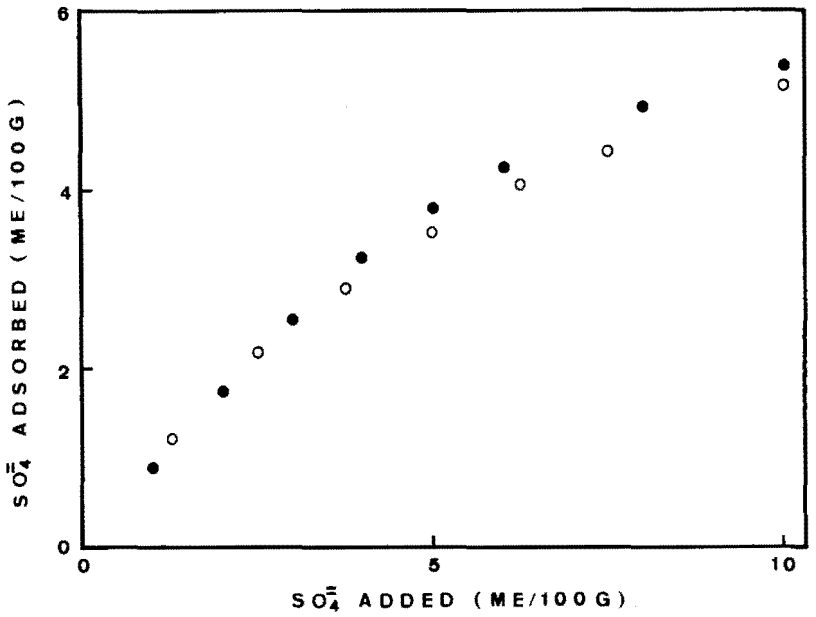

FIGURE 20. EFFECT OF CHLORIDE ON SULFATE ADSORPTION ON HILO (I-4) SOIL. SOLID CIRCLES REPRESENT SULFATE ADSORPTION IN THE ABSENCE OF CHLORIDE. OPEN CIRCLES REPRESENT ADSORPTION IN THE PRESENCE OF CHLORIDE. THE SUM OF THE SULFATE AND CHLORIDE ION ADDED WAS MAINTAINED AT 20 ME/100 GRAMS.

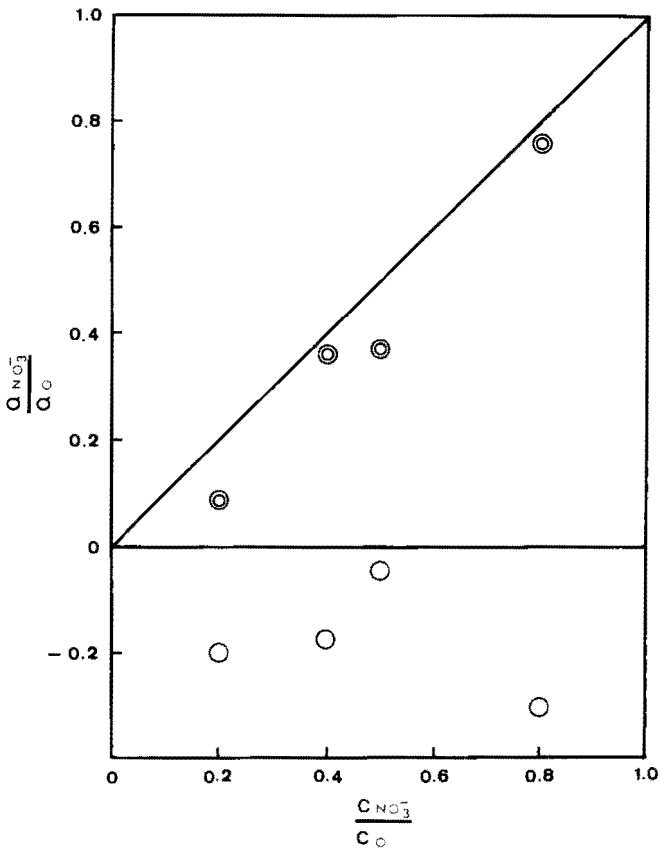

FIGURE 21. EFFECT OF CHLORIDE AND SULFATE IONS ON NITRATE ADSORPTION ON KCl-WASHED AND DIALYZED AKAKA (I-5) SAMPLE. THE TOTAL ANION CONCENTRATION WAS MAINTAINED AT 100 ME/100 GRAMS. (◎) REPRESENTS INFLUENCE OF CHLORIDE ION ON NITRATE ADSORPTION AND (○) REPRESENTS EFFECT OF SULFATE ION NITRATE ADSORPTION.

A most interesting result is obtained when adsorption from solutions containing a constant amount of sulfate but with varying amounts of nitrate is examined. Table XII shows data of this type. More sulfate is adsorbed at the higher nitrate concentrations. These data are consistent with the adsorption model proposed in this thesis. Since nitrate and sulfate ions are adsorbed through different processes (i.e., non-specific and specific), no direct competition for adsorption should occur. Increasing the concentration of an indifferent electrolyte at pH values greater than the zero point of charge results in a lowering of the pH with increasing electrolyte concentrations. This is the case as is shown in Table XII. Since sulfate adsorption is strongly pH dependent as shown by Chao et al. (1963, 1964), and further, lowering of pH renders the surface more negative, it is not surprising that more sulfate is adsorbed with increasing nitrate concentration.

The present adsorption model also predicts that less sulfate would be adsorbed with increasing indifferent electrolyte concentration at pH lower than the zero point of charge. There should be no effect of electrolyte concentration on sulfate adsorption at the zero point of charge.

If the situation is reversed, that is the nitrate concentration held constant and the sulfate concentration varied, adsorption of nitrate is strongly influenced by sulfate concentration. This effect is shown in Table XIII. Increasing the sulfate ion concentration progressively displaces the zero point of charge to lower pH values so that for a given pH one would expect the surface

TABLE XII. EFFECT OF INCREASING INDIFFERENT ELECTROLYTE (KNO_3) CONCENTRATION ON SULFATE ADSORPTION ON A KCl-WASHED PLUS DIALYZED HILO (I-4) SAMPLE.

$SO_4^=$ Added (me/100 g)	NO_3^- Added (me/100 g)	Equilibrium pH	Soil to Solution Ratio	$SO_4^=$ Adsorbed (me/100 g)
20	0	7.40	1:12.5	9.14
20	20	7.22	"	10.78
20	200	6.91	"	11.32
20	500	6.81	"	11.35
20	1000	6.70	"	12.40

TABLE XIII. EFFECT OF INCREASING SPECIFICALLY ADSORBED ANION CONCENTRATION ON ADSORPTION OF INDIFFERENT ELECTROLYTE ANION (KNO_3) ON A KCl-WASHED PLUS DIALYZED HILO (I-4) SAMPLE.

NO_3^- Added (me/100 g)	$SO_4^=$ Added (me/100 g)	Equilibrium pH	Soil to Solution Ratio	NO_3^- Adsorbed (me/100 g)
20	0	6.54	1:12.5	2.77
20	20	7.22	"	-0.72
20	200	7.15	"	-0.58
20	1000	7.13	"	-0.51

negative charge to increase accordingly, with a resultant decreasing attraction or increasing repulsion of nitrate ions. Increasing the sulfate concentration also increases the pH of the equilibrium solution, further contributing to the negative character of the colloid surface.

Note also that at pH's higher than the zero point of charge, increasing the concentration of an indifferent electrolyte lowers the pH, whereas increasing the concentration of a specifically adsorbed anion increases the pH. Adequacy of the anion adsorption model proposed in this thesis is evidenced by its ability to explain a host of apparently conflicting data.

SUMMARY AND CONCLUSIONS

Anions are adsorbed on soil colloid surface specifically or non-specifically. Specific adsorption involves exchange of the anion with ligands coordinated to lattice metal ions. Anions which are non-specifically adsorbed are retained as counter ions in the diffuse double layer opposite a positively charged surface.

Of the anions commonly added to soils as fertilizer, pesticide, amendment or filler, nitrate and most likely chloride ions are non-specifically adsorbed. Sulfates, phosphates, silicates, arsenates, molybdates, and many organic anions are specifically adsorbed.

Charge on oxide surfaces varies with the number and kind of adsorbed potential determining ions. In the pH range normally encountered in soils, H^+ and OH^- are the important potential determining ions. In the acid range the surface accepts protons and acquires a net positive charge. At high pH the surface loses protons and acquires a net negative charge. The pH at which net charge is zero is referred to as the zero point of charge.

When a solution containing an anion which is non-specifically adsorbed (indifferent electrolyte) is used to measure the pH of an oxide or soil, the pH will be higher in the salt solution than in water or a dilute solution in the pH range below the zero point of charge.

At pH values above the zero point of charge, the pH will be higher in water or dilute solution than in the concentrated solution. Delta pH (ΔpH) was defined as

$$\Delta pH = pH \text{ (electrolyte solution)} - pH_{H_2O}$$

or $\triangle$ pH = pH (high electrolyte conc.) - pH (low electrolyte conc.)

The sign of the $\triangle$pH value corresponds to the net charge on the colloid surface. The sign can be positive, negative or zero.

The quantity of non-specifically adsorbed anions retained as counter-ions depends on the net charge. One can expect little or no anions of this type to be adsorbed at pH above the zero point of charge.

Specifically adsorbed anions can enter into ligand exchange at pH well beyond the zero point of charge and their adsorption varies with the kind of anion. Adsorption of these anions also displaces the zero point of charge to lower pH, rendering the surface more negative. An anion which can render a surface negative is adsorbed to a greater extent than an anion which is less able to confer negative charge to this surface. Phosphates, for example, are more strongly adsorbed than sulfates because the former can render the surface more negative than the latter.

When phosphate is adsorbed by a surface, the increased negative character of the phosphated surface can be shown by a measurable increase in cation exchange capacity. As much as fivefold increase in cation exchange capacity has been demonstrated to occur with phosphate application.

The native sulfate content of Hawaiian soils is highly correlated ($r = 0.96$) to their sulfate adsorption capacity. Native sulfate content ranged from zero to 50.7 me per 100 gms, and sulfate adsorption capacity from zero to 84 me per 100 gms.

Anion adsorption capacity of oxide soils varies with pH, concentration, anion species and the surface nature of the oxide. In general,

adsorption increases with decreasing pH. However this is not always the case, for orthosilicate is known to be adsorbed more strongly at neutral pH than at low pH.

For a given pH and anion species, maximum adsorption is obtained, and anion adsorption is best described by the Langmuir equation.

At pH's near 6.5 about 1/7th as much sulfate and 1/25th as much nitrate is adsorbed relative to phosphate adsorption, when adsorption is expressed as millimole per 100 grams of soil. It is believed that in most cases anion adsorption might best be expressed as millimole per unit weight of soil since steric factors probably do not permit more than one bonding oxygen of a polyvalent ion to enter into coordination with the oxide surface.

The iron oxides of Hawaiian soils vary in their capacity to adsorb anions. Based on sulfate adsorption capacities of Hawaiian soils, estimates give sulfate adsorption capacities ten times greater in Hydrol Humic Latosols, per unit weight of oxide than in the remaining Great Soil Groups.

It is believed that a greater proportion of exchangeable ligands in the Hydrol Humic Latosols consist of aquo, hydroxo and ol groups, whereas soils developed under drier climate consist of oxo coordinated ligands. Colloid surfaces with a high proportion of oxo groups are not expected to adsorb many anions.

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